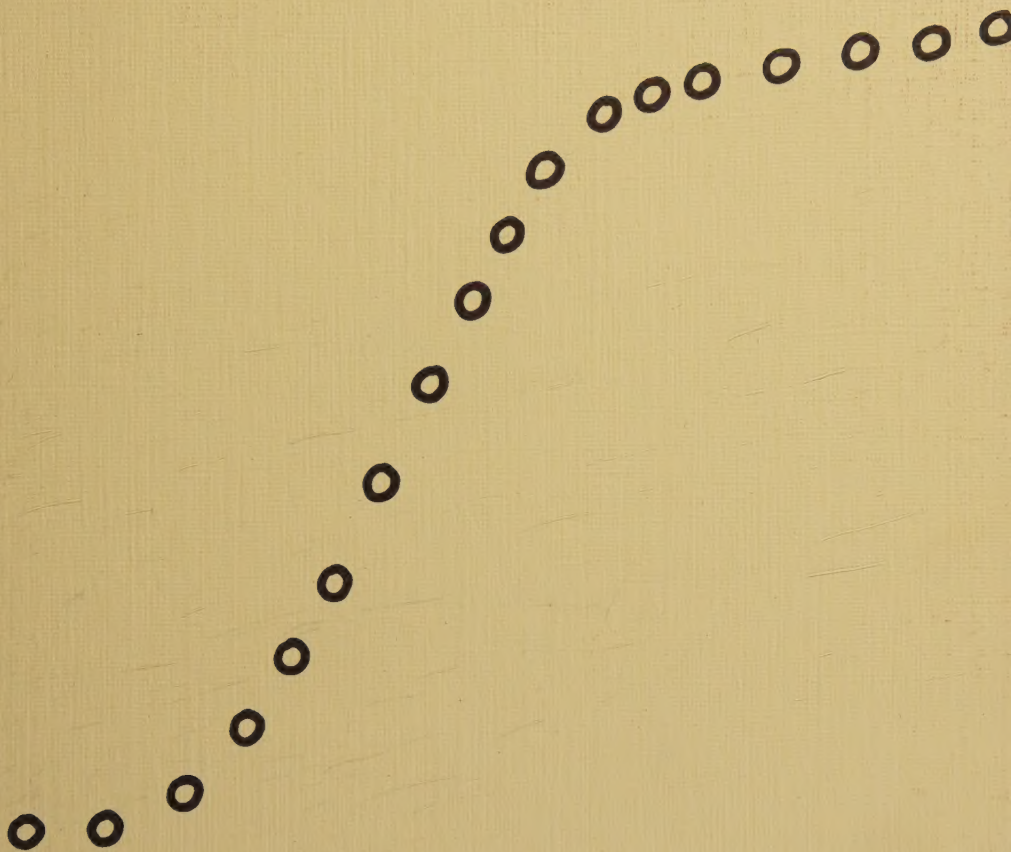




PROTON INDUCED X-RAY EMISSION AND γ -RAY ANALYSIS-

experimental arrangement and applications to work
environment aerosols

KLAS MALMQVIST

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PROTON INDUCED X-RAY EMISSION
AND γ -RAY ANALYSIS

by
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Title and subtitle Proton Induced X-Ray Emission and γ -Ray Analysis — Experimental Arrangement and Applications to Work Environment Aerosols.	
Abstract An analytical facility for <u>multi-elemental analysis</u> by <u>Particle Induced X-ray Emission</u> , PIXE, combined with simultaneous <u>fluorine analysis</u> by use of the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction, has been designed and evaluated. The facility is characterized by high flexibility to facilitate continuous implementation of new devices. The results of the testing show good overall performance with detection limits for elements heavier than phosphorous of the order of 10^{-10} – 10^{-8} g and 10^{-7} g for fluorine. A careful <u>mass calibration</u> procedure is presented and applied to the system. The precision and accuracy for thin samples are better than 5%. The <u>charge build-up</u> , associated with particle bombardment in non-conducting samples and which deteriorates the analytical performance, was eliminated by the insertion of a hot electron emitting filament. A system for <u>on-demand beam excitation</u> with the addition of a fast external electronic pile-up rejection circuit was implemented, yielding increased pulse count-rate capability, improved pile-up rejection and reduced target deterioration. The high capacity was exploited in a comprehensive study of the fumes from thirteen electric arc welding methods. The total mass and the elemental composition of the fumes depend strongly on the choice of welding process and of welding parameters, especially welding voltage. Mass median aerodynamic diameters for the particle size distributions vary from 0.3 to 0.6 μm . The chromium in fumes from shielded metal arc welding is almost entirely <u>Cr(VI)</u> while in <u>gas metal arc welding</u> it is <u>Cr(III)</u> .	
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SUMMARY

Introduction

During the last few decades, the rapidly growing concern about pollution in the environment has stimulated and initiated the development of an arsenal of techniques for sampling and analysis, applicable to environmental research. One very important part of our total environment is the work environment where we spend a substantial part of our lives. Furthermore, since in many work places a large number of different chemicals are found, normally in much higher concentrations than in the ambient environment where we spend our leisure hours, our total exposure to potentially hazardous substances is largely determined by our working conditions. The relationship between dose and effect has not yet been fully ascertained for many substances common in industry today and the intense technical development continuously introduces new processes and materials, which imply new potential risks.

The technique of Particle Induced X-ray Emission analysis (PIXE) has been shown to have a high potential in the study of airborne particles (aerosols) in the environment, as has been demonstrated frequently in investigations of ambient atmosphere (1,2). In the present work, the development of a PIXE facility and its application to work environment aerosols are described. The latter comprises a systematic characterization of the properties of the aerosols emitted during electric arc welding.

PIXE

In 1970, Johansson, Akselsson and Johansson (3) at our laboratory presented the first study of applying heavy charged particles to trace element analysis. Ever since then, the development of the method has continued in many laboratories all over the world and many new fields of applications have been established. The proceedings of the two International Conferences on Particle Induced X-Ray Emission and Its Analytical Applications, held at our laboratory in 1976 and 1980 (1,2), demonstrate the basic development and the broad spectrum of applications.

Similarly to other analytical methods based on detecting X-rays, PIXE makes use

of an exciting radiation to create vacancies in the inner shells of the atoms in a sample. When the vacancies are re-filled from the outer shells, the excess energy is emitted as X-rays or Auger electrons. By measuring the energy of the characteristic X-rays, the atoms from which they originate can be identified and by measuring the intensity of the X-rays quantified.

The exciting radiation may be photons (X-rays from an X-ray tube or a radioactive source), electrons (e.g. in a electron microscope) or heavy charged particles (from an accelerator) as in the case of PIXE. The latter radiation has several favourable properties which make it superior for many types of samples, e.g. lower detection limits and higher analytical speed are generally obtained.

In a typical PIXE analysis (see paper I) the sample is placed in a vacuum chamber and irradiated by charged particles from an electrostatic accelerator or a cyclotron. Protons or α -particles with energies from 1 to 4 MeV/u are used in most laboratories, although heavier ions may be used as well (4). The particle beam intensity is normally from 1 to 200 nA and analysis times from 1 to 3 minutes. The X-rays are measured with an energy-dispersive semi-conductor detector, e.g. a Si(Li) crystal, and the X-ray spectra stored in a multi-channel analyser. In routine analyses, 10 to 20 elements can be determined simultaneously with detection limits of the order of 10^{-9} g in thin (<1 mg/cm²) samples. Under special conditions (very thin targets with very high current densities) detection limits of the order of 10^{-12} g or even lower can be attained (2). In thick samples, the concentration detection limits are of the order of ppm. The accuracy and precision are for thin samples better than 5% (paper I).

Similar to other X-ray methods, the attenuation of low energy X-rays sets a lower limit to the atomic number and only elements heavier than phosphorous can be analysed quantitatively. In contrast to other X-ray methods, in PIXE light elements also can be analysed by making use of simultaneous particle induced nuclear reactions including elastically scattered particles. An element of significant hygienic interest, fluorine, has a very high cross section for proton induced gamma rays and in paper I the advantages of combining PIXE and the nuclear reaction $^{19}\text{F}(p,\gamma)^{16}\text{O}$ for simultaneous analysis are demonstrated.

Thesis

The work presented in this thesis was originally initiated about the time when an old Van de Graaff accelerator at our laboratory was replaced by a new 3 MV tandem accelerator (NEC UDH Pelletron). During the replacement period, work was started to develop a new experimental facility for PIXE (paper I-IV), with special concern to flexibility in combination with high accuracy and precision and high capacity for sample processing. The latter was required for the realization of planned major applicational studies implying the processing of thousands of multielemental analyses. Such a study is described in the last paper (paper V) of this thesis.

Paper I

In this paper is a detailed description and evaluation of a facility for simultaneous PIXE analysis and analysis of fluorine by the detection of gamma rays from the reaction $^{19}\text{F}(\text{p},\gamma)^{16}\text{O}$.

A stainless steel irradiation chamber has been constructed and fitted with externally exchangeable beam collimators and X-ray absorbers, an automatic system for sample changing exploiting standard slide frames and an electron gun for charge build-up elimination (paper III). An on-demand pulsed particle beam facility (paper IV) reduces pulse pile-up and sample deterioration and a diffuser foil is used to obtain a homogeneous beam profile. The chamber was intentionally designed as a rather large volume container to permit continuous upgrading and the implementation of new techniques. A thorough mass calibration procedure has been applied to the system (paper II) and its detection limits have been determined.

Apart from a Si(Li) detector to register the X-rays, a large volume NaI crystal was incorporated for the simultaneous detection of proton induced gamma rays from the $^{19}\text{F}(\text{p},\gamma)^{16}\text{O}$ reaction. The proton energy interval which gives the lowest overall detection limits in PIXE (2-3 MeV) coincides with an energy interval where the cross section for the production of the high energy gamma rays from this reaction is large. Furthermore the variation of the cross section is rather small and samples well-suited for PIXE analysis (thickness $< 1 \text{ mg/cm}^2$) can simultaneously be analysed for fluorine by gamma ray analysis.

Paper II

To fulfil the demands of high analytical accuracy and precision, a careful mass calibration of the analytical set-up was performed and followed by continuous checking of long-term stability by the analysis of a specially designed sample. The paper describes an approach implying the irradiation of several different single element standard foils of known thicknesses. The parameters of a physical model are adjusted to fit the experimental calibration curve. For the set-up described in paper I, the accuracy in the analysis of a random sample is determined to be better than 5%.

Paper III

When samples with very low electrical conductivity are bombarded by charged particles, charge build-up may occur and the sample potential reach several kV before discharging. Electrons will be accelerated towards the high potential and hit the sample. Intense electron bremsstrahlung up to an energy of several keV is produced and causes a high continuous background in the X-ray spectrum, thus severely increasing the detection limits.

To eliminate charge build-up, two different approaches are described in the paper. The first employs a battery operated electron emitting hot carbon filament to spray the samples with electrons and the second raised chamber pressure.

Paper IV

Due to the long shaping time constants in X-ray amplifiers, the pulse processing capacity is limited. When a large number of X-rays are detected per unit time, the count rate in the electronics will be high and the probability for partial or total addition of pulses significant. This addition causes distorted X-ray spectra and hence normally electronic pile-up rejector circuits (PPR) are employed in commercial X-ray units. The PPR eliminates essentially all pile-up except for the complete pulse addition which takes place when pulses are so close that the PPR, because of its non-zero pulse-pair resolution, cannot

separate them. Discrete pile-up peaks at the double (triple, etc) nominal energies are left in the X-ray spectrum.

When pulses are rejected by the PPR, electronic dead time results and has to be corrected for in quantitative analysis. At very high input count rates, apart from distortion of the X-ray peaks, the dead time will eventually reach 100% and no output will emerge from the X-ray electronics. These problems are avoided by using a system for fast removal of the particle beam as soon as an X-ray is detected and then maintaining the beam off the target during the processing of an event. With such a system it is possible to have a high output count rate without using high currents and very high input count rates.

In the set-up described in paper I, the particle beam passes between two condenser plates before reaching the target. By keeping a high voltage at the plates and letting an event in the detector trigger an electron tube which can promptly discharge one of them, the beam can be removed within a very short time and essentially no pile-up occurs. A fast external electronic PPR has also been used, to suppress further the double energy pile-up peaks.

Paper V

The analytical facility described in paper I - IV has been employed for the realization of a major applicational study of the properties of the fumes emitted during electrical arc welding. Thirteen different methods of welding have been investigated in a welding laboratory as to their total mass fume emission, elemental composition and particle size distribution. For stainless steel welding, the oxidation state and solubility of chromium were also determined. For each method, systematic variations of welding parameters (welding current and voltage) were performed to determine their influence on fume formation.

Altogether more than 3000 multi-elemental analyses were performed throughout the course of the study and PIXE was shown to be a very powerful method for the study of work environment aerosols. Large differences in fume formation between the welding methods were observed. The welding parameters influence the total mass emission as well as the elemental composition but seem to have little influence on particle sizes, which are normally well below 1 μm .

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A FACILITY FOR MULTIELEMENTAL ANALYSIS BY PIXE AND THE $^{19}\text{F}(\text{p}, \alpha \gamma)^{16}\text{O}$ REACTION

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Specific advantages with Particle Induced X-Ray Emission are: its 1) multielemental capability, especially when combined with nuclear techniques for lighter elements, 2) speed, 3) low detection limits for small samples and 4) accuracy. To make full use of these advantages, analytical parameters have to be chosen optimally and the facility to be carefully designed. This paper describes an experimental facility constructed to permit continuous development work to optimize the analytical conditions and to allow the gradual implementation of automatic control. Emphasis is also put on the simultaneous use of proton induced gamma rays from fluorine. The features and the performance of the set-up including its accuracy, precision and experimental detection limits are reported.

INTRODUCTION

Particle Induced X-Ray Emission, PIXE, has been a rapidly developing analytical technique over the last decade. Since 1970, when Johansson et al presented their pioneering paper,¹ PIXE has been applied in many different fields of science, e.g. atmospheric chemistry and medicine. Two International Conferences on Particle Induced X-Ray Emission and its Analytical Applications held at Lund in 1976 and 1980 have clearly demonstrated this development^{2, 3}.

To make extensive use of the specific advantages of PIXE, e.g. multielemental capability, speed, low detection limits for small samples and accuracy, appropriate experimental arrangements and procedures have to be developed.

As compared to other X-ray techniques, one of the major advantages of PIXE is the possibility of simultaneously using the information carried by nuclear reaction products including the scattered projectile particles and hence extending its analytical capability also to elements lighter than sulphur. The feasibility of using Particle Elastic Scattering Analysis (PESA) has been shown

at several laboratories^{4,5}. Most PIXE-laboratories, however, use 2-4 MeV protons which limits the usefulness of PESA to the analysis of major (light) constituents and to the determination of total sample mass⁶. The gamma rays from nuclear reactions are the other possible source of information on light elements. The advantages of using such gamma rays have been demonstrated in several articles^{7,8}.

Due to its high abundance in some common welding rods, fluorine may be found in high concentrations in air in work places, being sometimes the first element to exceed its hygienic threshold limit value. Particular interest in the characterization of welding aerosols at our laboratory⁹ has initiated the development of a procedure for analysing fluorine using the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction simultaneously with PIXE.

For studies of the fluorine depth distribution in various matrices the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction has been used extensively, making use of the resonance character of the cross section^{10,11}. In order to obtain the total mass of fluorine in samples of thicknesses from 0.1 to 1 mg/cm², e.g. in an aerosol sample on a filter from a work place investigation, it is necessary to have a yield of gamma rays per fluorine atom which is almost independent of the depth in the sample. As will be further discussed, protons with energies of about 2.5 MeV, which fortunately is also an energy well suited for PIXE analysis, can be used for this kind of analysis.

The design of the experimental set-up is crucial for optimal use of the speed, the low detection limits and the accuracy of PIXE. To facilitate continuous optimization, the set-up is characterized by flexibility and prepared for automatic control. This has been achieved at the price of increased complexity which introduces some extra concern about charge integration.

In this paper, the system for PIXE and fluorine analysis and its performance are described.

THE PIXE FACILITY

Basic design

The vacuum chamber of this facility for combined X-ray and gamma ray analysis is

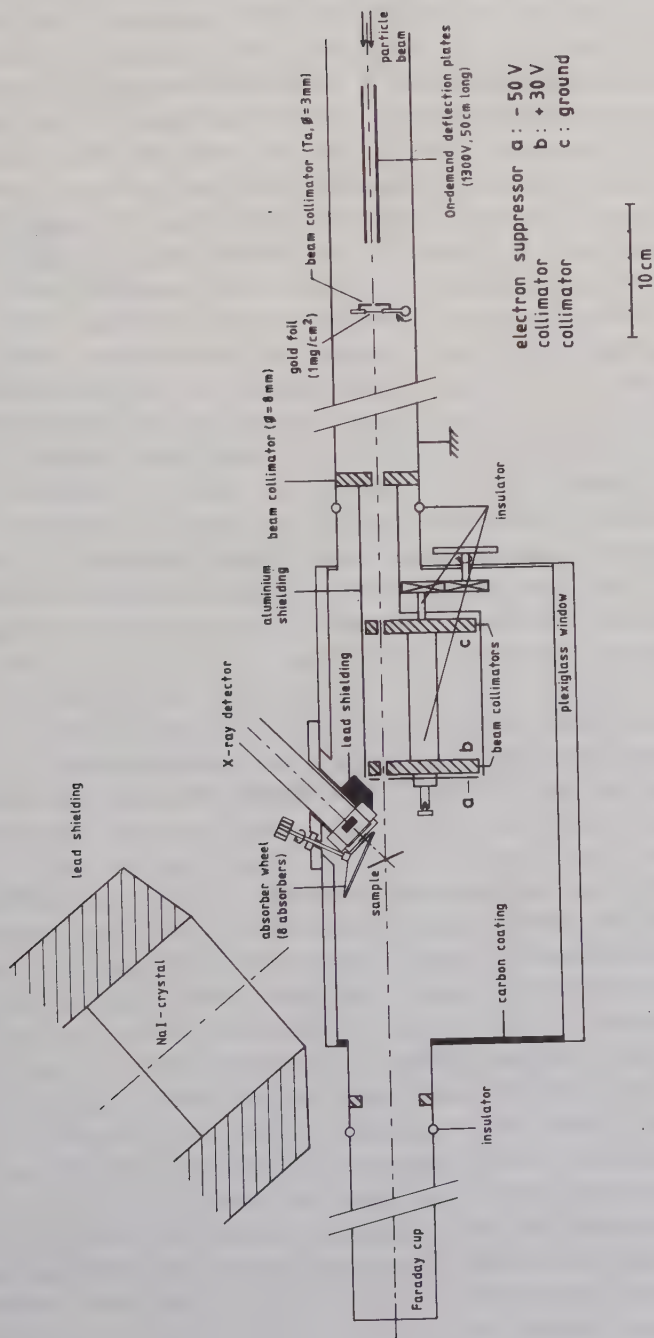


Fig. 1. Irradiation chamber for simultaneous X-ray and gamma ray analysis.

is shown in fig. 1. The size and shape of the chamber are partly determined by the demands for flexibility mentioned above. It is constructed from stainless steel and partly covered on the inside with carbon plates to reduce the characteristic X-ray background caused by scattered protons. On the top and the front walls exchangeable plexiglass windows allow observation of the interior parts. A "revolver" including ten sets of circular carbon collimators (table 1), each set consisting of a pair of collimators separated by 10 cm, allows the selection of a proper beam diameter from outside the chamber. The choice of beam diameter depends on the type of sample and the specific analytical task. Between the target and the last collimator a secondary electron suppressor ($U = -50$ V) is inserted to prevent the escape of electrons from the charge measurement region. The collimator revolver is shielded from the irradiation chamber by a grounded aluminium foil. In order to achieve a proton beam with a constant intensity distribution over its entire cross section, the beam is passed through a thin gold foil (1 mg/cm^2 , gold evaporated on to glass plates and then floated off on water and fixed to a frame) situated 0.6 m before the target. This foil represents a compromise between having a homogeneous beam at the target and the consequent reduction in beam intensity (about a 15-fold reduction for 8 mm beam diameter). Since with this beam diameter it is anyhow possible to obtain a current of 200 nA at the target, this intensity reduction does not represent a severe limitation.

A Si(Li)-detector (Kevex, sensitive area: 80 mm^2 , crystal thickness: 5 mm; resolution: 158 eV at 5.9 keV) is inserted into the chamber wall, at 135° relative to the beam (which gives a lower intensity of electron bremsstrahlung than at 90° , ref.¹²) with a distance of 0.040 m between the target and crystal. To maintain vacuum (better than 10^{-4} torr) but allow low energy X-rays to leave the chamber, a window ($110 \mu\text{m}$ beryllium) is attached between the detector window ($25 \mu\text{m}$ beryllium) and the target. The large variety of analytical situations places considerable demands on a proper choice of X-ray absorber and hence a wheel fitted with 8 different X-ray filters (see table 1) allows the insertion of an absorber suitable for the specific analytical situation. A stainless steel compartment beneath the chamber, designed for the $5 \times 5 \text{ cm}^2$ standard photographic slide frames which are commonly used at many PIXE laboratories, contains a slide tray taking 40 samples. This compartment is evacuated before the valve, separating the container from the chamber, is opened, thus minimizing the time wasted due to pumping. By electro-pneumatic remote control, a sample is positioned in the proton beam and after analysis automatically replaced by using computer steering. The sample changing procedure can be checked over a closed-circuit television network.

Table 1

Beam collimators: diameters (mm) : 1, 3, 4, 5, 7, 8, 9, 10, 12

X-Ray absorbers:

<u>material</u>	<u>thickness (μm)</u>	<u>hole (%)</u>
Mylar	77	—
Mylar	340	—
Mylar	340	1.66
plexiglass	1110	—
aluminium	53	0.12
aluminium	152	—
aluminium	154	1.78
aluminium	310	(x)

(x) Double layer absorber made from two 155 μm aluminium foils, one with 4.3% and one with 0.06% relative hole areas. The foils are put together with coaxial holes. This absorber is specially designed for the analysis of geological material⁸.

Table 1. Diameters of the beam collimators and specifications of the X-ray absorbers which can be selected in the set-up discussed.

With a sample in position for analysis, the sample mounting frame (aluminium) automatically makes electrical contact with the chamber. This facilitates the charge transport, especially from thick samples, thus reducing the risk of charge build-up. However, for highly insulating thick samples, local positive voltages may reach several tens of kilovolts before electrical discharges occur and due to the acceleration of electrons towards the positively charged sample, a significantly increased electron bremsstrahlung background will occur in the X-ray spectrum. To avoid this, a battery operated carbon filament is used to spray the sample with electrons¹³. The use of a closed battery circuit prevents the introduction of false currents which might spoil the current integration. The latter is made using a current digitizer (ORTEC 439) and a scaler to count the number of charge pulses. For very low currents (< 2 nA), special precautions are necessary so as not to disturb the current measurement. No one is allowed to move close to the set-up, since changes in the chamber capacitance may be

induced. Further careful grounding of surrounding equipments and electronics is required to reduce induction of currents.

X-rays produced in the sample by proton (2.55 MeV) bombardment are detected in the Si(Li) crystal producing signals which after passing a preamplifier enter an X-ray amplifier (Kevex 4525P) and a fast leading edge discriminating system (ORTEC 474 + ORTEC 406A). Pulses from this system trigger an on-demand beam deflection device¹⁴. About 400 ns after the detection of an X-ray event an electron tube (PL 519) grounds one of two parallel plates, normally kept at 1300 V and situated about 0.7 m up the beam line. The sudden electric field between the two plates deflects the proton beam from the target and keep it off while the X-ray amplifier is busy processing the X-ray event (for an 8 μ s amplifier time constant the processing time is approximately 80 μ s). Due to this on-demand beam system, radiation damage, sample heating and pulse pile-up are reduced and the electronic dead-time is insignificant. The system is routinely operated together with the electronic pulse pile-up rejector of the X-ray amplifier to reject any events arriving while the beam is off.

After shaping and stretching in the X-ray amplifier, the pulse is fed to an analog-to-digital converter and then stored in a computerized multichannel analyzer (Nuclear Data 6620). The spectrum evaluation is done with the HEX computer code¹⁵ comprising non-linear least squares fitting. To improve the accuracy and to allow for the use of high count rates (up to 5000 cps), the code has been implemented with corrections for Si-escape peaks and pile-up peaks¹⁶.

The system calibration for quantitative PIXE analysis¹⁷ is determined by the repeated irradiation of 45 homogeneous single element standard foils of accurately known elemental masses (the accuracy of individual foils is stated to be better than 5%, ref.¹⁸). Careful measurements or estimations of physical parameters, e.g. sample-to-detector distance, detector crystal dead-layer thickness etc., are used to attain an initial calibration. A calibration curve is fitted to the measured elemental yields with special attention to the physical interpretation and by comparing it with the estimated initial calibration. This procedure is then repeated iteratively.

To determine the accurate thicknesses of the X-ray absorbers, they are calibrated by analysing suitable homogeneous samples with and without the respective absorbers. For absorbers with hole (to transmit part of the low energy X-rays), the solid angle of the holes are determined by irradiation of a

low-Z element sample with and without the absorbers. The efficient beam area of each collimator is determined by analysing a spot-sample of accurately known elemental mass. For further details regarding the calibration procedure, refer to ref.¹⁷.

The requirements for high sample processing rates are taken care of by preparing the set-up for computer control. At present, sample changing is made automatically and both beam collimators and X-ray absorbers are designed for remote control via stepping motor drives.

Charge measurement

The number of protons incident on the target is integrated by use of a current digitizer and to check its accuracy, a high impedance ($R_i = 1000$ megaohms) voltmeter was used to measure the voltage over a 10 megaohms precision resistor (inaccuracy below 0.1%). For currents higher than 10 nA the inaccuracy of the digitizer is below 0.5 % and for currents between 1 and 10 nA below 1 %. Hence, even at low beam currents, the inaccuracy of the digitizer will be insignificant.

The current integrator is normally connected to the irradiation chamber as well as to the Faraday cup. Measurements show that for 2.55 MeV protons in this special set-up and for the total thickness of sample and substrate exceeding 3 mg/cm² it is necessary to collect the charge from the chamber as well as that from the Faraday cup. Unless this is done systematically a low charge will be measured, due to scattering of particles in the sample.

When striking the target, the protons will produce secondary electrons and some of those produced near to the surface of the material are emitted from the sample. The relative yield of such electrons will depend on proton energy and sample composition¹⁹. The total charge of these electrons has to be measured for accurate charge integration. To avoid the escape of the electrons through the last collimator, a negatively biased electron suppressor is inserted between it and the sample. In fig.2 the number of K X-rays per measured charge from an infinitely thick silver plate is plotted versus the negative bias of this suppressor. From the plot it can be inferred that at least -20 V is required in this special arrangement for accurate charge integration (the bias normally used is -50 V).

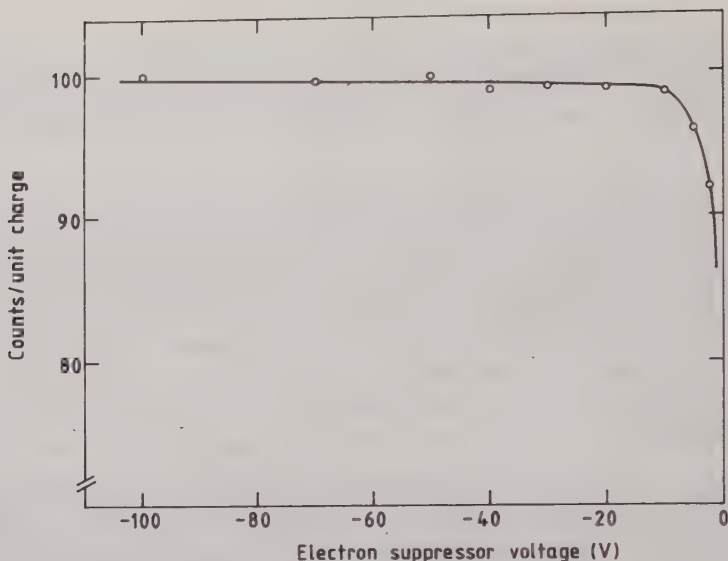


Fig. 2. Numbers of Ag K X-rays per measured charge (arbitrary units) from a thick silver plate plotted versus the negative bias on the electron suppressor. The proton current was 2 nA.

Due to the scattering of protons in the first collimator, some protons will hit the second collimator although this has a slightly larger diameter than the first one. To keep the secondary electrons produced in the last collimator from reaching the region of charge collection, it is kept at a positive voltage (+30V, empirically determined).

For accurate results the number of X-rays per unit charge should remain constant for different proton currents. To check for this, samples were analysed with varying currents and in fig.3 the number of Cu K X-rays per measured charge are plotted versus current for an infinitely-thick carbon pellet.

Since very low proton currents (1 to 5 nA) are occasionally used, the analysis will be very sensitive to erroneous extra currents. The on-demand beam system¹⁴ uses an electron tube for rapid grounding of one of the deflection plates. This system is a strong emitter of electromagnetic radiation, which may be picked up by parts of the current measurement system, thereby inducing extra currents in the nanoampere range. This can be checked with no beam on the target and an X-ray source on the detector to simulate normal count rates in the beam

deflection system. To avoid such currents, only coaxial cables are used and their shields are connected to ground at several points. There may also be other reasons for additional currents and this is an important problem worth much attention from any user of large irradiation chambers anxious to perform accurate ion beam analysis.

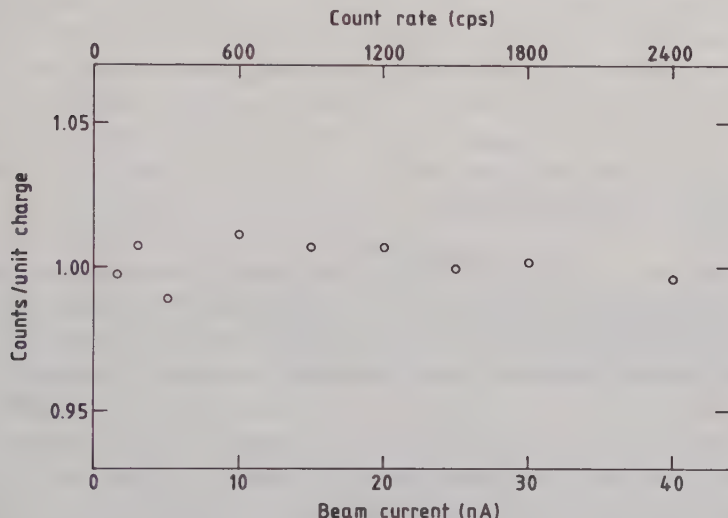


Fig. 3. Numbers of Cu K X-rays per unit charge (arbitrary units) versus proton beam current and count rate, when bombarding an infinitely thick carbon pellet. The statistical uncertainty in each determination is less than 1%.

Proton beam performance

The homogeneous current density over the beam cross section required for the analysis of small inhomogeneous samples is obtained by a diffuser foil. Such an arrangement causes a significant reduction in beam intensity as compared to the use of the electrostatic proton beam sweeping technique. The latter, however, has at least one significant disadvantage for the analysis of inhomogeneous samples: a well focussed beam of high intensity, swept at a kilohertz frequency over the sample, may induce a rather low average count rate, but can intermittently give rise to high rates. Since the probability for pulse pile-up

is proportional to the square of the instantaneous count rate, possible high local concentrations of elements present in an inhomogeneous sample will, in case of proton beam sweeping, cause enhanced pulse pile-up in the spectrum.

To check the beam homogeneity, the beam mapping method²⁰ has been applied. First, the beam is focussed and steered through the sample centre and then a diffuser foil (gold foil; 1 mg/cm^2) preceded by a small tantalum collimator (diameter: 3 mm) is inserted into the beam. To be able to reproduce its position, horizontal and vertical micrometer gauges are used. A small piece of copper foil was fixed to a polymer foil (Kapton, thickness $7.5 \text{ }\mu\text{m}$) and moved horizontally and vertically stepwise in the plane of the sample through the beam with an 8 mm diameter. The number of X-rays (Cu K_α) was registered and normalized to the beam charge collected. In fig. 4a is shown the beam intensity distribution in the vertical direction.

For small samples, e.g. impactor samples, the measured numbers of X-rays will vary with their horizontal positions in the homogeneous beam because of the varying solid angle relative to the detector. In this case it is feasible to use a skew beam intensity profile with lower intensity at the side closer to the detector. In fig 4b. the horizontal beam intensity distribution has intentionally been made skew so that the measured number of X-rays is approximately constant. For comparison, the result of a beam scan with a homogeneous beam is also shown (broken line). This solid angle effect is still more pronounced when the X-ray detector is at right angles relative to the beam and with small distance between the sample and the detector. In these cases the solid angle changes relatively more with position for small samples. In the experimental set-up discussed here, a skew beam profile is used routinely.

The theory of multiple scattering by Meyer²¹ may be used for comparison with experiments and as a guide for designing a suitably-skew beam profile. Figure 4a shows very good agreement between theory and experiment.

The collimator pairs are made from carbon, the second one being somewhat larger than the first one so as to reduce the number of protons scattered out of the beam which would otherwise form a low intensity halo around the beam core. The use of the beam mapping method outside the the beam core shows that, for a beam diameter of 8 mm, the current density of the halo 2 mm from the edge of the core is less than 0.1% of the core density. To reduce this further, the collimators are at present being replaced by tantalum collimators of anti-scatter design²².

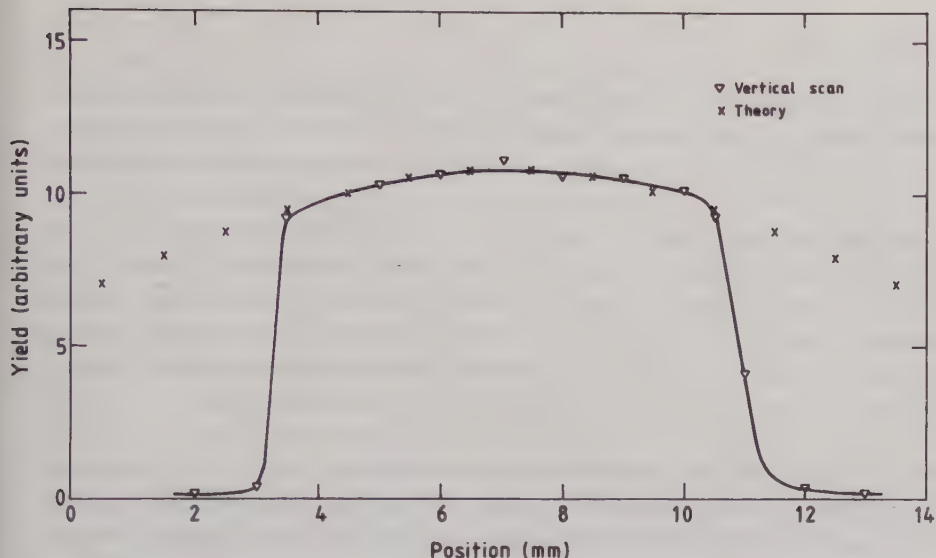


Fig. 4a. Experimental proton beam intensity profile in the horizontal (o) direction in the sample plane as measured by the beam mapping method²⁰. The beam collimator was 8 mm and the undiffused beam passed through the sample centre. For comparison, a theoretical profile based on the calculations by Meyer²¹ is also given (x).

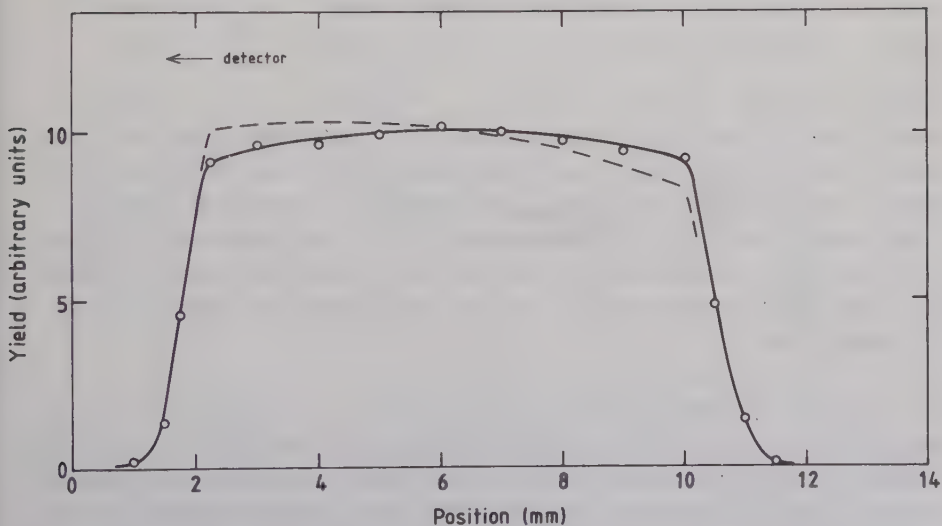


Fig. 4b. Horizontal beam scan for a skew beam intensity. The arrow points to the side closer to the detector. Small samples representing the same mass arbitrarily scattered over the beam cross section will in this case each yield approximately the same intensity. For comparison, a beam scan for a homogeneous beam is also given (broken line).

Detector effects

Particles scattered in the sample may, in cases when either none or a very thin X-ray absorber is used, reach the Si(Li) crystal with an energy of several hundreds of keV left. In such cases an event of very high energy is deposited in the detector. Frequent resets may occur in the optical feedback system of the preamplifier and severe distortions of the X-ray spectrum are obtained, e.g. peak broadening and peak centroid shift. Such effects render the X-ray spectra unsuitable for computer analysis and in severe cases may even render quantitative analysis impossible. This problem is avoided in the present set-up by using a beryllium foil of 110 μm thickness as window in the target chamber and thus still maintaining good transmission for low energy X-rays.

Similar distortions are also observed when bombarding certain kinds of targets, mainly those containing high concentrations of fluorine, e.g. aerosol filters made of Teflon fibres and some geological materials. The distortions are found even if a very thick absorber is used between the target and the detector. In these cases, high fluxes of gamma rays causes intermittent high (>1 MeV) energy depositions. This has been checked independently by analysing an X-ray spectrum and a gamma ray source (^{60}Co) simultaneously, obtaining the same kind of distortion of the X-ray peaks. Since the Si(Li) crystal cannot be shielded from gamma rays from the target position, samples producing an intense flux of high energy gamma rays have to be avoided. In some cases, it may be possible to select a proton energy having a low cross section for gamma ray production.

A significant background continuum in the X-ray spectrum is caused by gamma rays produced when the protons strike the collimators and then Compton scatter in the detector crystal²³. This yield is in particular significant when very thin targets with low intrinsic production of gamma rays are irradiated. By applying a lead shielding to the Si(Li) detector (see fig 1), the background for high X-ray energies is reduced by about 50% for 2.55 MeV protons and carbon collimators. By exchanging these for tantalum collimators, the background would be further reduced.

When X-rays are incident on the Si(Li) crystal close to the edge of the sensitive volume, incomplete charge collection may take place due to the distorted electric field pattern near the edge. As a result, the pulse height registered will be somewhat lower than the nominal pulse height from such an event. These degraded X-ray events form a low energy tail to the corresponding

full energy peak²⁴. This introduces difficulties in peak area determinations and an increased background for lower energy peaks riding on the tail. The effect can be reduced at the expense of reduced detector solid angle by inserting a collimator in front of the crystal and thereby preventing the X-rays from interacting in the poor electric field region.

The 80 mm² detector in this set-up is collimated to an approximate efficient sensitive area of 30 mm² by a tantalum collimator in front of the detector window. This reduces low energy tailing significantly as can be seen by comparing spectrum a and spectrum b in fig 5a. However, there is a significant residual tail which may cause slight problems in computer spectrum analysis. By bringing the detector bias to zero and then directly back again to its normal voltage (-1000 V) a significant decrease of peak tailing is achieved as can be seen in spectrum c in fig 5a. To check the time variation of the tailing after applying the detector bias, a ⁵⁵Fe-source was placed 10 mm in front of the detector (without collimation). The detector bias was applied and then pulse-height spectra were recorded after different times. In fig 5b the spectra are superposed, showing the gradual increase in peak tailing with time. When a

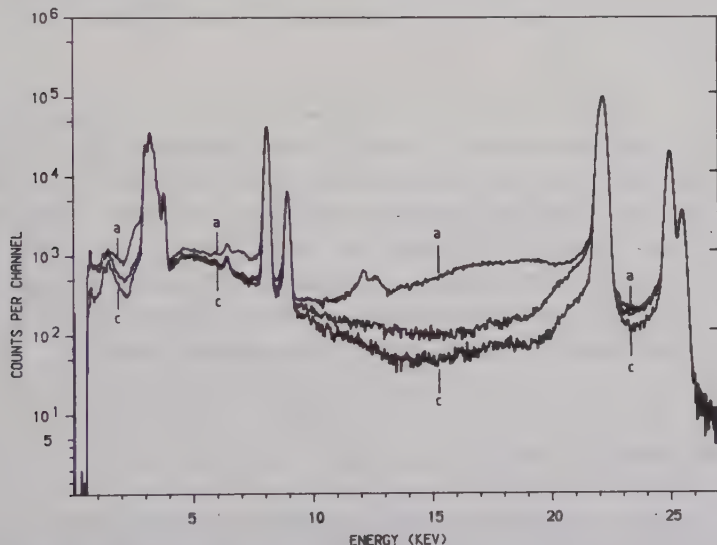


Fig. 5a. X-ray spectra from bombardments of a thick silver plate. The beam diameter was 8 mm and an external X-ray absorber of 340 μ m mylar was used. The total accumulated number of counts is the same in all three cases. In spectrum a, the whole Si(Li) crystal area (about 80 mm²) was exposed to the X-rays and in spectrum b, a tantalum collimator was placed outside the Be-window of the detector thus reducing the effective crystal area to 30 mm². In spectrum c, a temporary further reduction in low energy peak tailing was obtained by removing and immediately reapplying the detector bias.

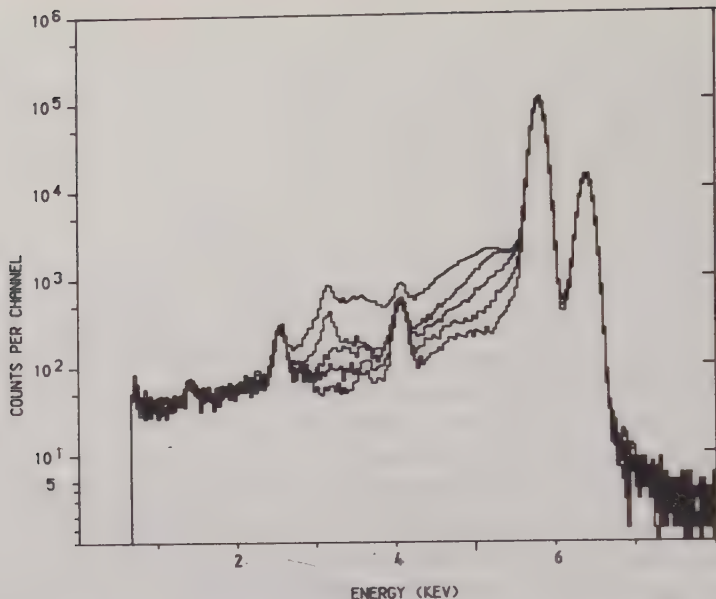


Fig. 5b. Pulse-height spectra from a ^{55}Fe source accumulated at different times after applying the detector bias. The Si(Li) detector was uncollimated and the total numbers of counts in the spectra are the same in all cases. The spectra refer (from bottom to top) to measurements at 0, 20, 60, 120 and 700 minutes after application of the bias.

small collimator is used and thus X-rays only are incident at a small central part ($\approx 10 \text{ mm}^2$) of the sensitive area of the detector, the peak tailing is as low as in case of a recently applied voltage. A tentative explanation for these effects is that, at least for the detector discussed, the on/off-procedure of the detector bias increases the charge collection efficiency in the poor electric field region at the crystal edge. Nothing has been found about this phenomenon in the X-ray detector literature and presumptive customers are advised to pay some attention to this effect when purchasing detectors.

Calibration and detection limits

In ref.¹⁷ the mass calibration of the PIXE system is described in detail. The accuracy in the determination of random elements is estimated to be better than 5% and is still better for ratios of elements. This accuracy refers to the routine analysis of an unknown thin sample.

To check the stability of this mass calibration, a quality control sample has

been run with each batch of samples (< 40 samples). By repeated analyses (800 times) of this sample over a year, the long term stability for homogeneous samples is shown to be better than 2.5% and for inhomogeneous samples better than 4% (one S.D.).

Detection limits for PIXE analysis are sensitive to the experimental conditions. To illustrate the capability in routine analysis of the PIXE arrangement described, interference-free mass detection limits were determined in the following way: A thin polystyrene foil (about $30 \mu\text{g}/\text{cm}^2$) was bombarded by a 150 nA proton beam with a diameter of 8 mm. The total accumulated charge was 40 μC . A 75 μm Mylar X-ray absorber was used. The detection limits were calculated as the mass corresponding to $3\sqrt{B}$ pulses, where B is the number of counts in the background within an interval of ± 2 S.D.s around the Gaussian peak (see fig 6).

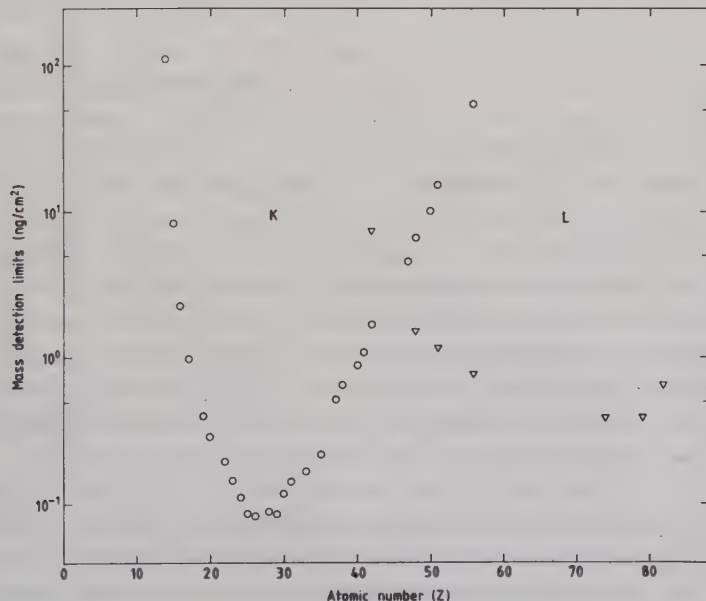


Fig. 6. Experimental mass detection limits versus atomic number calculated assuming no interference between adjacent lines. A 8 mm diameter beam was used to irradiate a thin (about $30 \mu\text{g}/\text{cm}^2$) polystyrene foil with few minor impurities. The total accumulated beam charge was 40 μC and an external X-ray absorber of 75 μm was used. The detection limits have been calculated as the mass which corresponds to $3\sqrt{B}$ pulses, where B is the background area below ± 2 S.D.s of the Gaussian X-ray peak in question. o and ∇ are determined for K- and L-lines respectively.

FLUORINE ANALYSIS

Physical principles and proton energy

When ^{19}F nuclei are bombarded with protons of MeV energies there is a high cross section for nuclear reactions forming $^{20}\text{Ne}^*$ -nuclei in excited states. The $^{20}\text{Ne}^*$ -nuclei de-excite by alpha particle emission to excited states in ^{16}O , which de-excite promptly to the ground level by the emission of gamma rays with energies 6.13, 6.92 and 7.12 MeV respectively²⁵. Due to the high energy of these gamma rays, they easily penetrate the walls of the irradiation chamber and can be detected by an external gamma ray detector.

The cross section of the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction as a function of proton energy E_p has a pronounced resonance character²⁶. Very sharp and high resonances for the production of the three gamma rays occur at $E_p = 0.873$ MeV, $E_p = 1.347$ MeV and $E_p = 1.374$ MeV. For E_p in the interval 2.0 to 2.6 MeV the sum of the intensities of these gamma rays (see fig. 7) shows a fairly smooth energy dependence remaining at a high value of cross section and, if the initial proton energy is selected to lie in the 2.0 to 2.6 MeV region and if the protons, after passing the sample, emerge with an energy above 2.0 MeV, the variation in gamma ray yield in the matrix will be less than $\pm 20\%$ (see fig 7). For the integrated matrix yield, the variation is still less and it is rather simple to correct for these small variations if the approximate sample thickness and composition are known. In the proton energy interval from 2.0 to 2.6 MeV the cross sections for proton induced gamma rays in other light nuclides are negligible compared to that in fluorine²⁷ and since the gamma lines (6.13, 6.92 and 7.12 MeV) are virtually free of interfering lines²⁷, the yields from possible competing reactions can be ignored.

Protons with energies of 2 to 3 MeV are the optimal projectiles for PIXE analysis^{28,29,30} and suitable sample thicknesses are up to 1 mg/cm^2 since such samples yield low background radiation and the results do not normally require corrections for particle slowing-down and X-ray absorption. Further, protons in the energy range 2.2 to 2.6 MeV are slowed down less than 0.2 MeV for these sample thicknesses and hence protons in this energy interval can advantageously be used for simultaneous PIXE and fluorine analysis.

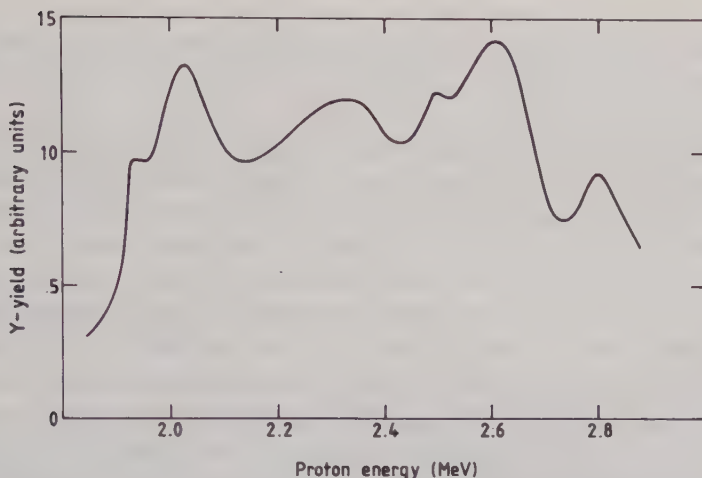


Fig. 7. Yield of high energy gamma rays from the reaction $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$ in a thin target versus proton energy (after ref.^{2,6}).

Experimental arrangement

To match the low detection limits possible with PIXE, a large volume detector is preferred for the high energy gamma ray detection. Since no interference of any significance is expected, a large sodium iodide crystal is a good choice.

The practical detection limits are set by the background radiation. The material in collimators, chamber walls, etc., may contain substantial amounts of fluorine and will also be continuously contaminated with fluorine during the bombardment and handling. Since $^{19}\text{F}(p, \alpha\gamma)^{16}\text{O}$ reactions take place in the material of the experimental set-up with significant solid angle relative to the detector and since these high energy gamma rays have a high probability of penetrating material on their paths to the detector, their intensities will determine the practical lower limits of detection attainable in a specific analytical system.

Hence, careful design and choice of material is essential to keep the proton induced background radiation low. It is also essential to shield carefully the gamma ray detector from the natural background radiation emanating, e.g. from the concrete walls of the laboratory, since this could otherwise increase the detection limits.

In our set-up 2.55 MeV protons are used and the high energy gamma rays are detected in a 5x4" NaI crystal positioned at a distance of 0.15 m from the

target. Thick (0.06 m) lead shielding is incorporated around the cylindrical detector crystal (see fig 1).

For routine analysis, simple and convenient recording is obtained by a scaler with a lower level discriminator adjusted to count pulses referring to gamma rays produced in the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction only. The discriminator adjustment is carried out using a multi-channel analyser in the gating mode to set the discriminator level just below the double escape peak. The scaler is stopped after a preset accumulated beam charge. The number of counts normalized to the accumulated charge gives a relative yield, Y_s , for the known standard sample with a fluorine content C_s (mass per unit area). The blank substrate which is used to carry the fluorine standard is then irradiated giving another relative yield, Y_{sb} , which is subtracted from Y_s to get the net fluorine yield for the standard. To improve the accuracy of the calibration, several homogeneous standard samples with different fluorine compounds are normally analysed.

The unknown sample, containing the fluorine mass C_u per unit area, is then irradiated similarly to the standard foil, giving a net yield of Y_u . From an analysis of the substrate, Y_{ub} is obtained. Since different samples may be analysed for varying lengths of time and often significantly longer than the standard samples, the influence from natural background radiation should preferably be corrected for as well. This background component is dependent on the collection time and is essentially independent of the accumulated beam charge. Consequently all counts have to be reduced by t times Y_{bt} , where t is the real analysis time and Y_{bt} the number of background events per unit real time. The mass of fluorine per unit area can then be calculated from the following simple formula:

$$C_u = C_s \cdot (Y_u - Y_{ub}) / (Y_s - Y_{sb}),$$

where $C_s / (Y_s - Y_{sb})$ can be the average result from several standard samples. If very high count rates are used, significant electronic dead-time occurs and has to be corrected for.

In our set-up the beam passes through a diffuser foil to permit the analysis of heterogeneous samples. In this foil about 95% of the protons are scattered from their initial direction and out of the beam hitting tube walls and collimators, all of which are more or less contaminated by fluorine. A substantial number of gamma rays will thus be produced here and contribute considerably to the number

of fluorine counts. If, however, a well-focussed beam is used without any diffuser foil (as is possible for homogeneous samples) and deposited in a Faraday cup far away from or well shielded from the NaI crystal (see fig 1), the relative contribution of gamma rays due to scattered protons is significantly reduced. The absolute lower level of detection is then improved by more than one order of magnitude (for this particular experimental configuration).

Performance and Discussion

The samples most commonly analysed at our laboratory are aerosol samples between 0.1 and 1 mg/cm^2 in thickness. Assuming homogeneous samples it is possible from proton stopping power data³¹ and the yield curve in fig.7 to calculate the integrated relative fluorine gamma ray yield as a function of sample thickness. This function is slowly varying and also slightly smoothed by the energy straggling, which takes place when the protons pass through the matter. The integrated yield from a sample is rather insensitive to the sample composition. In fig 8 the integrated yield of gamma rays from the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction, without any corrections for straggling, are plotted versus sample thickness for three different matrices for an initial proton energy of 2.55 MeV (corrections for straggling would change the yield less than $\pm 2\%$ over the energy and thickness intervals in question). For samples thinner than 3 mg/cm^2 a crude

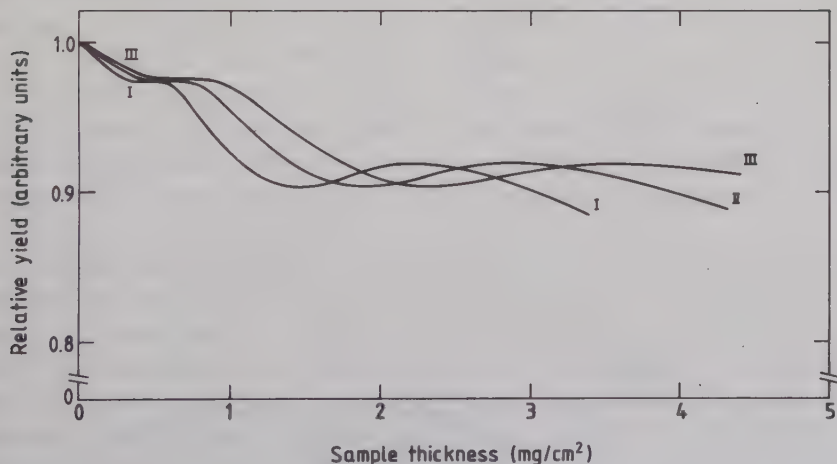


Fig. 8. Integrated relative yield of gamma rays from the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction versus sample thicknesses for three different matrices: I) 100 % C, II) a welding aerosol matrix composed of 17% O, 20% F, 8% Si, 20% K, 10% Ca, 3% Mn and 22% Fe and III) 100 % Fe. An initial proton energy of 2.55 MeV and homogeneously distributed fluorine have been assumed.

estimation of the sample thickness (better than $\pm 20\%$) and of the sample composition facilitates a simple and accurate correction for sample thickness in fluorine analysis. The accuracy of the correction factor is estimated to be well within $\pm 5\%$. If the sample is not homogeneous, e.g. after sampling an aerosol with time-dependent composition, an estimation can be made from fig 7 to check for possible inaccuracies. Using a proton energy of 2.55 MeV and samples (welding aerosol matrix) thinner than 1 mg/cm^2 with all the fluorine in the first 0.1 mg/cm^2 or in the last 0.1 mg/cm^2 of the sample respectively gives errors of less than $+10\%$ and -10% respectively compared to the assumption of homogeneously distributed fluorine.

The dependence on thickness was checked experimentally by analysis of filters with different loadings of welding aerosols of constant composition. The samples were irradiated by 2.55 MeV protons and the yields normalized to the beam charge collected. In fig.9, the fluorine mass per unit area as determined by the procedure reported is plotted versus the aerosol sample thickness as determined gravimetrically. The circles represent values corrected for the sample thickness of the welding aerosol matrix (see fig 8). If no corrections at all are made, the maximum deviations from the solid straight line in fig 9 will still be less than 10% .

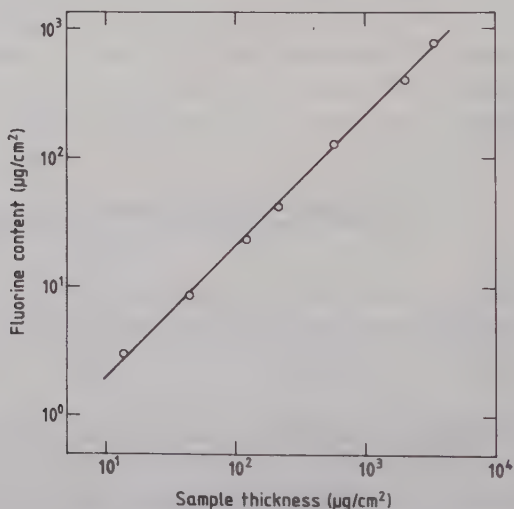


Fig. 9. Fluorine mass per unit area as determined by the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ method versus the gravimetrically determined sample mass density. Welding aerosol samples of different thicknesses but the same composition (identical to the one in fig 8 II)) were used.

The lower limits of detection for analysis with the $^{19}\text{F}(\text{p},\alpha\gamma)^{16}\text{O}$ reaction depend on the probability of producing gamma rays, i.e. on initial proton energy and on sample thickness. Further system parameters, e.g. solid angle and efficiency are important. The detection limits will, however, also be depending partly on the intensity of gamma rays produced outside the sample and strongly on the proton beam characteristics and the surroundings of the beam.

If no diffuser foil is used and the beam is well-focussed so as not to hit the collimators, the absolute mass detection limit is at the same level as those of routine PIXE analyses for heavier elements. By irradiating known masses of a fluorine salt solution pipetted on to Nuclepore filters, the experimental detection limit has in this way been estimated to be 5 ± 3 ng fluorine within the beam area (about 2 mm^2). This rather low detection limit is only applicable to the analysis of homogeneous samples which do not require a homogeneous beam. The detection limit has been defined as the mass corresponding to 3 times the S.D. of the average yield from five blank Nuclepore samples.

For homogeneous beam irradiation, the detection limit is of course more dependent on the geometrical arrangement around the beam and on the shielding of the gamma ray detector. Sample carrying substrates, e.g. filters, vary considerably in thickness and hence the divergence due to multiple scattering when passing through the substrate varies with its thickness. Such scattering of the beam can have a slight influence on the level of background radiation. For routine analysis of samples collected on membrane filters (Nuclepore, thickness: 1 mg/cm^2), the detection limit in this particular set-up has been determined to $100\pm 25\text{ ng/cm}^2$. While being somewhat high compared to PIXE detection limits, this limit is quite sufficient for most applications. In welding aerosol samples, the fluorine mass per unit area is normally 10 to $200\text{ }\mu\text{g/cm}^2$.

The absolute analytical mass determinations are based on a comparison with homogeneous reference fluorine samples of known mass. The accuracy will then depend on the accuracy of the latter samples. The manufacturer states better than 5% accuracy¹⁸ for an individual foil and the accuracy may be further improved by the analysis of several different standard foils and using the average calibration value. In addition to this, errors are introduced because of inaccuracies in the charge integration when irradiating the sample and the standards and because of uncertainties in the corrections for proton slowing-down when the sample's thickness and composition are not accurately

known. The accuracy of the method has been checked experimentally by the analysis of known samples and by comparison with a standard procedure for fluorine analysis.

A very common analytical method for fluorine assaying, e.g. in welding aerosols, is to dissolve the sample followed by determination of the concentration of fluoride ions (F^-) in the solution with a fluoride ion selective electrode³². Only that part of fluorine which is soluble in the solvent used is analysed.

A comparison between the ion selective electrode and the $^{19}F(p,\alpha\gamma)^{16}O$ technique was performed with seven membrane filters, homogeneously loaded with welding aerosols of varying thickness. Each filter was cut in two equal parts, one of which was irradiated with protons and quantified according to the standard foil method described above. The welding aerosol on the second half was dissolved in 20 ml of distilled water and analysed with an ion selective electrode. For higher filter loadings, the solutions were diluted 10 to 25 times before analysis to avoid saturation of the electrode caused by excessive fluoride ion concentrations.

The seven filters (Millipore, diam: 37 mm, pore diam.: $0.8\mu m$) were loaded with amounts from 0.1 to 5 mg of welding aerosol (electrode ESAB OK 48.00) collected on to areas of about 8 cm^2 . A comparison of the results between the two methods of analysis gives an average ratio of $^{19}F(p,\alpha\gamma)^{16}O$ to ion selective electrode results of 1.05 ± 0.04 ($\pm$ one standard error of mean). This is close to unity and within the 5% accuracy for the reference samples stated above. However, the somewhat lower results for the ion selective analysis may be explained by incomplete dissolution of the fluorine from the welding aerosol due to the existence of a fraction of less soluble fluorine compounds. Most fluorine in the fumes from normal low hydrogen coated electrodes is water soluble due to the presence of alkali metals such as Na and K^{33} but sometimes the rather insoluble fluorine compound CaF_2 may also be present in the fume. The $^{19}F(p,\alpha\gamma)^{16}O$ method is not dependent on the chemical form of the fluorine and is further able to analyse nondestructively over a large mass interval. Hence it is very well suited for the analysis of aerosol samples in combination with PIXE analysis.

The precision of the method is mainly determined by the pulse statistics. For a homogeneous sample, the relative standard deviation attained with repeated analyses of the same samples was determined to be 1.5%. The uncertainties due to pulse statistics were less than 0.7%.

Simultaneous X-ray and gamma ray detection

The earlier mentioned possibility of a combination of PIXE and gamma ray detection for fluorine analysis is of great importance. This combination has been tested by irradiation of samples pipetted on to Nuclepore filters. A 1 g/litre stock solution of the salt K_2TiF_6 was used to prepare solutions of known concentrations. Using 5 μ l micro-pipettes, 5 to 20 μ l of the various solutions were pipetted on to filters thus obtaining spot samples with known elemental masses of F, K and Ti. The samples were analysed simultaneously for K and Ti by PIXE analysis and for fluorine according to the technique earlier described. In fig 10 the elemental masses determined are plotted versus masses calculated from known concentrations, volumes and the stoichiometry of the chemical compound. For samples well above the detection limits, the statistical uncertainties due to pulse counting were below 1%. Possible inaccuracies in the sample preparation procedure may account for part of the uncertainty.

The solid line represents the ideal slope 1.00. The correlations between the determined and calculated masses are excellent for all three elements ($r^2 > 0.9997$). For titanium and potassium, the slopes are 0.95 ± 0.01 and 1.02 ± 0.01 respectively and for fluorine 1.08 ± 0.02 (1 one S.D.). From the error limits given, one can infer that only part of the deviations from the ideal line can be explained by the rather high uncertainties for low elemental masses close to the detection limits. The absence of experimental values for fluorine below 100 ng is due to the absolute mass detection limits being relatively higher than those of PIXE analyses. Although several sources of uncertainty are present, the good accuracy and agreement between the two methods show the analytical combination of PIXE and gamma ray counting for fluorine to be very versatile and powerful extending the analytical capability of the ion beam facility to an important element without increasing irradiation time.

In the section "Detector effects" above, it is shown that problems may occur when X-rays are detected in the Si(Li) crystal if simultaneously an intense flux of MeV gamma rays are incident on the crystal. Consequently, if a very large amount ($> 1 \text{ mg/cm}^2$) of fluorine is present in the sample being analysed, it will be difficult to simultaneously perform PIXE analysis using the procedure described. For the sample thicknesses discussed above ($< 1 \text{ mg/cm}^2$) and normal concentrations of fluorine from below 1% up to a few tens of per cent, this will not be a problem.

CONCLUSIONS

The analytical arrangement developed constitutes an accurate and precise instrument for rapid multielemental analyses. Protons with energies of about 2.5 MeV, which in most applications give optimum general sensitivity for PIXE analysis, can be used for simultaneous and simple analysis of fluorine in thin samples ($<1 \text{ mg/cm}^2$) by detecting the high energy gamma rays from the reaction $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$.

The irradiation chamber comprises an automatic sample changing system based on commercial slide frames, externally exchangeable X-ray absorbers and proton beam collimators, on-demand beam pulsing, beam diffuser foil and an electron emitting carbon filament for charge build-up reduction. Careful mass calibration and testing of the different components have been carried out and the set-up shows good overall performance and long term stability.

The impact of protons and intense fluxes of MeV gamma rays on the X-ray detector give distorted X-ray spectra. To avoid proton impact, a rather thick (110 μm) Be-foil is used as chamber window. To improve the X-ray spectra, the Si(Li) crystal has been collimated from 80 mm^2 to 30 mm^2 effective sensitive area thus reducing low energy peak tailing due to incomplete charge collection. Removing and reapplying the detector bias reduces low energy tails of X-ray peaks temporarily.

From comparisons with a standard method for fluorine analysis (ion selective electrode) and proton irradiation of samples with known masses of fluorine, potassium and titanium, it can be inferred that counting the gamma rays from the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction is an accurate and precise technique for fluorine analysis of thin samples, e.g. in aerosol samples, and that it can preferably be combined with simultaneous PIXE analysis.

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CALIBRATION AND LONG-TERM STABILITY OF A PIXE SET-UP

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A general mass calibration procedure of a PIXE set-up is described. As an example, the results of the calibration of the PIXE set-up in Lund are given. For the calibration commercially available standards were used. The parameters of a physical model were adjusted to fit a calibration curve. To decrease errors due to inhomogeneities of the standard foils, the average from four different pieces of each foil was taken. The accuracy of the calibrated system in Lund is estimated to be better than 5% for individual elements and still less for ratios of adjacent elements.

For long-term quality control of the results, a special sample has been designed. This consists of a thick silver plate with a small copper spot in the centre. It is very sensitive to small changes in a PIXE set-up. By analysing this sample periodically, mistakes in the arrangement are promptly detected—a feature which is much appreciated in a mixed research, development and routine analysis laboratory. Also a measure of the long-term stability is obtained. For the Lund system, the long-term stability is 2.5% for a homogeneous sample and 4% for a small (inhomogeneous) sample.

1. Introduction

One important advantage of the PIXE-method compared to many analytical methods is the possibility of quantitative analysis without using standards. It is, however, initially necessary to establish a reliable calibration of the analytical system. This calibration may be performed in different ways. One approach is to procure accurate values of all the individual physical parameters of the system. Another way is to determine a sensitivity factor for each element of interest by fitting a calibration curve to experimental values. The second calibration procedure probably gives more accurate results than the first one if many good accurate standard foils are used. The second procedure is also less time-consuming.

In the Lund PIXE laboratory, we use mainly a calibration procedure suggested by Akselsson et al. [1]. In this procedure, we try to minimize the uncertainty of the calibration by using a physical model to guide the fitting procedure in the second method.

To maintain high analytical quality, it is important not only to have an initially accurate calibration but also to secure good stability of the experimental arrangement. This can be made by periodically analysing samples sensitive to any significant changes in the system.

2. The PIXE arrangement in Lund

Since the Lund PIXE set-up will be used as an example in the following discussions, a short description of the set-up will be given. For routine experiments, 2.55 MeV protons from a 3 MV Tandem accelerator (NEC 3 UDH) are used. For maximum flexibility in the set-up a large irradiation chamber was constructed (fig. 1). The chamber was used both for routine analysis and for developments of the PIXE-method. One disadvantage of a spacious chamber, however, is the more complicated charge integration required. In our system, we integrate the beam current both on the chamber itself and in a Faraday cup. To get an accurate charge integration, we use a secondary electron suppressor system, applying +30 V to the last collimator and –50 V to the electron shield between the sample and the last collimator (see fig. 1). For routine purposes, we recommend a smaller chamber.

A homogeneous beam is obtained by using a thin (~ 1 mg/cm²) gold-foil to diffuse the beam, and the beam-diameter may be varied from 1 mm to 1 cm by external collimator control.

The X-rays produced are detected in an 80 mm² (collimated to an effective area of 30 mm²) Si(Li) Kevex detector with an energy resolution of 158 eV at 5.9 keV. Instead of an ordinary pile-up rejector, we use an on-demand beam deflection system giving a pile-up interval of 300–400 ns.



Fig. 1. The PIXE set-up in Lund.

A surface barrier ring detector to measure back-scattered particles and a NaI-crystal for gamma-ray detection are also included in the system (fig. 1).

To avoid charge build-up on thick insulating samples, a battery operated electron emitting carbon filament [2] is located close to the sample.

3. Calibration procedure

The possibility of access to a certain type of accelerator and also the kind of samples to be analysed determine the kind of charged particles selected for PIXE-analysis. In the PIXE set-up in Lund, we use mainly 2.55 MeV protons. The proton energy has been calibrated using the 1.374 MeV (p, γ)-resonance for fluorine, by irradiating a thin CaF_2 -target evaporated on to a thick tantalum plate. The accuracy of the energy calibration is better than 10 keV.

3.1. Irradiation chamber performance

Before performing a mass calibration, it is necessary to test the linearity of the X-ray yield as a function of the count rate as well as of the accumulated charge. Fig. 2 shows the results of two such linearity tests of our system. Sample I has been irradiated using a moderate current (0.1–25 nA) giving count rates between 20 and 6000 c/s. For sample II, lower count rates (200–1300 c/s) and higher beam currents (10–65 nA) were used. No significant variation in the yield is found when the current is varied. When the count rate is increased a slight decrease in the

yield seems to occur. The difference between the maximum and minimum values is, however, only about 3%. To reduce pile-up peaks which could interfere with characteristic peaks in the spectra, most samples are analysed with a count rate below 2000 c/s. The maximum value of the current selected depends on the heat resistance of the sample irradiated and on the volatility of possible elements in the sample.

3.2. Calibration of thin, homogeneous samples

For the mass calibration, thin homogeneous and commercially available standards can be used. For our set-up, standards from MicroMatter Co were used [3]. These consist of a thin layer of the element of interest evaporated on to a Nuclepore filter. According to the manufacturer the accuracy is better than 5%.

The standards were analysed using a 0.53 cm² beam area and no external absorber except for the chamber window (Be). The count rates were all below 2000 c/s to reduce pile-up peaks in the spectra and the time of analysis was chosen to give a statistical error well below 1%. Altogether 45 different standard foils have been analysed for their K-lines. The stan-

Table 1

A list of the standard foils supplied by MicroMatter Co during 1977–1979. The standard compound is evaporated onto a Nuclepore filter.

Compound	Year of purchase	Compound	Year of purchase
Al	1977	As	1977
SiO	1979	CsBr	1977
GaP	1978	CsBr	1979
CuS	1977	RbNO ₃	1979
CuS	1979	SrF ₂	1977
CuS	1979	Y	1979
NaCl	1979	Nb ₂ O ₃	1979
KCl	1978	MoO ₃	1977
CaF ₂	1979	Ag	1979
Ti	1979	Ag-Hg	1979
V	1977	Cd	1978
Cr	1979	Sn	1977
Mn	1977	Sb	1978
Mn	1979	BaF ₂	1977
Fe	1978	BaF ₂	1979
Co	1979	WO ₃	1977
Ni	1977	Au	1978
Zn	1979	Pb	1979
		ThF ₄	1977
		UF ₄	1979

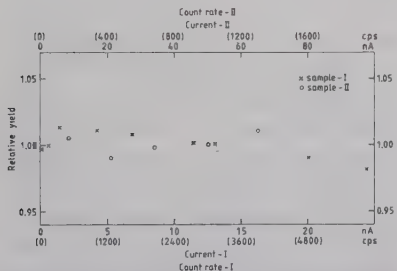


Fig. 2. Tests of the linearity of the X-ray yield (normalized to the mean) as a function of the beam current and the count rate for two different samples. The statistical error is less than 1%.

dards from the period 1977–1979 (see table 1) have been divided into four different pieces and all pieces have been analysed. The average value was used for the calibration.

A procedure often used in obtaining a calibration curve is to fit a nice-looking curve to the measured values and thus achieve sensitivity factors (counts/ $\mu\text{C}/\text{ng}$) for all elements [4]. We use a somewhat different approach in which the physical interpretation is stressed.

For our calibration, we use the formula:

$$A = c \cdot N / (P \cdot S \cdot T),$$

A = the mass per unit area of the element analysed (ng/cm^2),

c = a known constant ($0.00334 \times \text{atomic weight of the element}$),

N = the number of pulses in a peak per unit of charge [$(\mu\text{C})^{-1}$],

P = the X-ray production cross section in the peak (b),

S = the solid angle (sr),

T = the system efficiency.

To make a preliminary calibration, the X-ray production cross section is calculated from good results in the literature (e.g. from refs 5, 6 and 7). From simple measurements, the best possible estimates of the physical parameters of the analytical system (distance sample–detector, detector area, window thicknesses, thickness of gold and dead layer of the crystal, air gap and depth of the sensitive volume) are made.

Standards producing K-peaks of medium energy (4.5–17.5 keV) are used to determine the solid angle (S). The results for these elements are rather insensitive to small errors in the estimation of the system efficiency (T). We also check that the value of the solid angle determined is comparable within the uncertainties in the previous estimations of the distance detector–sample and of the area of the detector (total uncertainty <20%).

From results for lighter standard elements (1.5–4.5 keV), we determine the transmission through the system by making small changes of the used values of the window-thicknesses until we get by linear regression a horizontal line in fig. 3 in this energy region. By changing the value of the depth of the sensitive volume, the calibration for the heavier elements ($Z = 43\text{--}57$) can be varied. Since the depth of the detector is about 5 mm, the system efficiency for the heavier elements is relatively independent of small variations in this value. A change in the depth of the sensitive

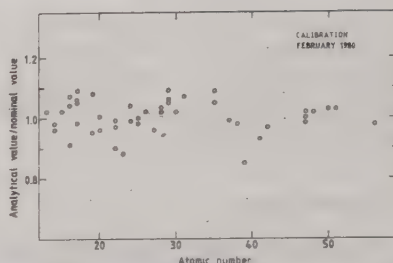


Fig. 3. The final results from the analyses of the standard foils divided by the values given by the manufacturer as a function of atomic number.

volume of the detector from 5 mm to 4.8 mm decreases the system efficiency by less than 1% for 30 keV X-rays.

Fig. 3 shows the results of the calibration after adjusting the physical parameters. The standard deviation of the mean is 0.8%. The following parameter values are used in our model: distance sample–detector 4.0 cm, detector area 0.28 cm^2 , chamber window $109 \mu\text{m}$ Be, air gap 0.4 cm, detector window $25.4 \mu\text{m}$ Be, gold layer $40 \mu\text{g}/\text{cm}^2$, dead layer $0.3 \mu\text{m}$ Si and depth of the detector 0.5 cm.

The manufacturer guarantees the stated thickness of each individual foil to be within 5% of its true value. The scatter of the results for adjacent elements as shown in fig. 3 indicates and further information from the manufacturer supports the supposition that any systematic component in the stated uncertainties is small. The error in the calibration due to uncertainties in the thicknesses of the standard foils is thus much smaller than 5%. Systematic errors in, e.g. cross section determination, charge integration and computer fitting of X-ray spectra all cancel out in the calibration procedure. If, however, any systematic errors occur only in part of the X-ray energy interval, they will remain. Such errors might be due to, e.g., local errors in cross section determination, incorrect estimation of the thickness of the detector gold layer or inhomogeneities in the detector crystal. The calibration curve in fig. 3 will give an estimate of the magnitude of this type of error. The accuracy of the calibration of a random element is estimated to be better than 5%. This estimation has been confirmed independently by Carlsson et al. [8], who used this calibration and thick target correction factors to obtain concentrations of several elements in some U.S. Geological Survey rock standards.

For heavier elements ($Z > 57$), the L-lines are used for mass calculation. To be able to calculate masses from different spectra containing L-lines using our fitting program [9], the relative intensities of the L-lines must be determined. This was performed by analysing thin single-element foils without any significant contaminations. By fitting the different peaks independently, their relative intensities can be determined.

The X-ray cross sections of the L-lines are not well-known and rather few elements have been analysed. Therefore a standard foil of each element of interest was analysed and the results used to determine a sensitivity factor for each element. The uncertainty of the calibration in this case depends directly on the accuracy of the single standard foil and due to outliers may exceed 5%.

3.3. Calibration of small thin samples

To carry out quantitative analyses using the PIXE-method, it is necessary to have either a homogeneous sample or a homogeneous beam. When small samples (smaller than the beam area) are analysed, it is important to use a homogeneous beam. In our system the homogeneity of the beam is obtained by letting the beam pass a small collimator (3 mm diameter) followed by a thin gold foil (about 1 mg/cm²). The distance between the diffuser foil and the sample is about 55 cm. To check the homogeneity of the beam profile, a small Ni-sample (diameter ~0.3 mm) is scanned step-wise over the beam cross section [10].

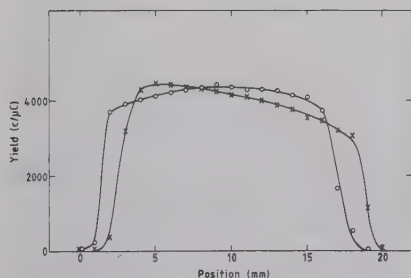


Fig. 4. The figure shows two vertical scans of the beam profile. A small (diameter ~0.3 mm) Ni-sample has been used for the scans. In the first scan (○), the beam was on the cylinder axis of the accelerator tube (see fig. 1). In the second scan (×), the beam was about 3 mm off the axis.

Two vertical scans are shown in fig. 4. As can be seen from the figure, it is important that the undiffused beam hits the centre of the sample [11]. To guarantee this, the beam is collimated and steered so as to hit the sample centre. Without moving the beam, the gold foil is turned into the beam allowing the beam to pass the small collimator in front of it. The exact position of this collimator relative to the sample should then be maintained and is checked using micrometer gauges, horizontally and vertically. To attain increased homogeneity of the beam, it is possible to use a thicker gold foil or to increase the distance between the sample and the foil. Both these modifications will, however, decrease the beam intensity. The degree of beam homogeneity desired has to be weighed against beam intensity.

To be able to obtain quantitative results for a small sample from the mass calibration, the beam area has to be determined. By pipetting 5.00 μl of a standard solution (1.00 g of the element dissolved in 1.00 l of distilled water) on a Nuclepore filter, small and thin standard samples are prepared. The accuracy of an individual sample is better than 5%. From bombardment of these standard samples, the beam area for each collimator can be determined.

4. Homogeneity test of standard foils

The area of the standard foils used is about 11 cm² which should be compared with the area analysed (0.53 cm²). If the standards are not homogeneous, this could introduce uncertainties into the calibration. When only a few standards are used for the calibration, this becomes especially important. All our standard foils, which were supplied by MicroMatter Co during the period 1977–1979 (see table 1), have been cut into four different pieces. All four pieces have one after the other been analysed with PIXE to check the homogeneity of the foils and, as mentioned above, to obtain a good estimate of their mean thicknesses. The beam current used when irradiating the standards has to be kept low to avoid losses of material or deterioration of the standard backing material. We normally used currents in the range 1–10 nA and a beam area of 0.53 cm². The maximum value of the proton current used on any standard foil was 20 nA. For the lighter elements (lighter than As), the irradiation time was typically around 100 s. An increase in the irradiation time was necessary for the heavier elements to get good statistics in

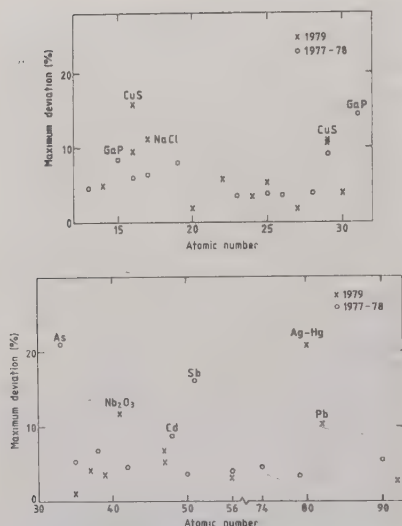


Fig. 5. The inhomogeneity of the different standard foils. The foils have been cut into four different pieces. In the figure is shown the maximum deviation (the maximum value minus the minimum value divided by the mean) in percent for different standards. For a single PIXE-analysis of a piece of a standard foil, the error due to statistics is less than 1%.

the peaks. When the same sample is analysed several times, the standard deviation is normally less than 1%.

In fig. 5 we have plotted the difference between the maximum and the minimum values of the separate pieces of a single standard foil as a percentage of the mean of all four pieces. For most of the foils, the deviation is in the range that might be expected but some outliers with a deviation of about 10% or more are present. The standard foils showing the largest deviations among their different pieces are GaP, CuS, NaCl, As, Nb₂O₃, Cd, Sb, Ag-Hg and Pb.

Using evaporation techniques when manufacturing standard foils may sometimes introduce a significant difference in thickness between non-adjacent areas of the foils. Since the thickness given by the manufacturer is an average value for the whole foil, our procedure of averaging the values obtained from the centre of each quarter of the foil is quite reliable. This statement is supported by the good agreement between the calibration values obtained in this way

(except for arsenic) from the less homogeneous standard foils and the values obtained from homogeneous standards of neighbouring elements.

However, there is another pitfall—the risk of losses of material due to the analysing technique used. Some of the parts of the standard foils used had been bombarded prior to this investigation which further accentuated this risk in our case. Repeated bombardments of foils revealed marked losses of arsenic and mercury (the silver of the Ag-Hg foil is not affected) in our experimental conditions. The extreme values for arsenic and mercury in fig. 5 may thus be explained by losses. The inhomogeneities of the NaCl, Nb₂O₃ and Pb foils are probably not accounted for by losses of material since the pieces of each foil which were earlier irradiated gave the highest values. The arsenic value was excluded from the calibration curve in fig. 3.

In other circumstances, the risk of loss of some elements other than As and Hg may constitute a problem, e.g., in calibration procedures using more damaging beams or using fewer different kinds of foils. Further investigations of losses from standards are currently in progress.

5. Quality control and long-term stability

It is very important for the users of all analytical methods to maintain good analytical quality. A well-calibrated system is not sufficient to guarantee this. Frequent checks of the stability and accuracy of the system must also be performed, e.g., by periodically analysing suitable samples.

For this purpose, a sample (or samples) which is quickly analysed and sensitive to significant changes of the analytical system should be used. It is also very important that simple errors due to operator oversight are rapidly detected. It is also important that the sample withstands all kinds of treatment without deteriorating, in order to make it possible to analyse the same sample over a long period of time. In our laboratory, MicroMatter standards (CuS) were originally used for quality control. We soon discovered that the standard backing material (Nuclepore) became fragile when irradiated for a period of time and that the standards were then easily damaged during handling.

The standard sample we have used for the last two years is made from a thick (1 mm) silver plate with a small piece (diameter ~1 mm) of copper foil in its centre. When analysing it, a beam current of 2 nA (count rate 2000 c/s) and a beam area of about 0.5

Table 2

The table shows probable explanations for different changes in the results from the analysis of the Ag/Cu-standard.

	Reason
All peaks changed:	Inaccurate charge integration. Detector badly positioned. Beam deflection system not working. Wrong secondary electron suppressor voltage.
One peak changed:	
Ag-L	X-ray transmission changed. Wrong angle between the sample and the detector.
Cu-K	Inhomogeneous beam. Collimator diameter not correct.
Ag-K	Wrong proton energy. Detector not working properly.

cm² are used and a 340 μ m Mylar foil is placed between the sample and the detector. To get a small statistical uncertainty (<1%) in the peaks of the spectrum, an irradiation time of 1 min is sufficient. The silver standard is analysed routinely before and after every batch of 40 samples and has so far been analysed more than 800 times.

In the spectrum from this Ag/Cu-standard, there are low energy peaks (Ag-L), medium energy peaks (Cu-K) and high energy peaks (Ag-K). In table 2, different patterns of changes in the areas of the peaks and their possible explanation are listed. When all peaks are changed by the same factor, it is often due to some error in the current integration. This error could be caused, e.g., by a leak current to or from the sample chamber or by not applying the correct voltage to the electron suppressors. Since a low current (2 nA) is used for the analysis of the sample, small variations in the charge integration can easily be detected. If the beam deflection system is not working, this gives a decrease of about 10% in all the peaks. Another reason for this kind of shift is a change in the solid angle, e.g., due to an incorrectly positioned detector.

When a variation mainly in the Ag-L peaks is detected, this is probably due to a change in the transmission of the X-rays. This kind of variation may also be due to a small change of the angle between the sample and the detector. A change of 5° from the normal angle of 22.5° gives a 7% error in the Ag-L peaks. The variation of the Ag-K peaks is then less than 1%.

If we find a change only of the Cu-K peaks, this is

probably due to beam inhomogeneity or because the beam area has been changed, e.g., by using the wrong collimator.

Finally, if the Ag-K peaks vary more than the other peaks, the reason may be that the proton energy is not correct. A proton energy of 2.65 MeV instead of 2.55 MeV gives an increased value for the Ag-K peaks of about 7%. Another explanation for the variation may be that the X-ray detector is not working properly.

We have also studied the long-term stability of our analytical system. The silver value (homogeneous sample) has a stability of 2.5% (= 1 standard deviation) over a one year period. The variation of the copper value for the same period was 4%. The larger variation for a small sample (spot) could be explained by changes in the homogeneity of the beam, as discussed earlier.

The variation over a long period should be compared with the variation when the sample is analysed several times during a short period (<3 h). The latter variation is less than 1%.

6. Conclusions

In the mass calibration procedure described, a fitting technique based on a suitable physical model is used. Another technique often used for calibration is direct fitting of a calibration curve to the measured values. One important advantage in using any fitting procedure is that single outliers of the results from the standard foils will have less impact on the calibration. Reasons for such outliers may be mistakes introduced during production or analysis of the standard foil, inhomogeneities of the foil or losses of standard material in the beam.

By using a physical model to guide the fitting procedure, errors due to incorrect standards in some part of the X-ray energy region can be further decreased. Especially when few standards are used, the direct fitting technique is very sensitive to the quality of the standard foils, and single outliers may introduce significant errors in the calibration. After having applied the calibration procedure described to our set-up, we estimate that an individual element can be analysed with an accuracy of better than 5% for elements with atomic numbers between 13 and 57 detected by their K-X-rays.

If only part of the available standard is analysed and rather few standards are used for the calibration, an additional error may be introduced due to inho-

mogeneities in the standards.

To maintain high quality in the analytical results, frequent controls of the calibration have to be made. A very versatile method for these tests of the stability, is the use of a thick silver plate with a copper spot. This sample is very sensitive to small changes in the analytical arrangement and withstands normal treatment without any noticeable deterioration. The long-term stability of the PIXE system in Lund is 2.5% for homogeneous samples and 4% for inhomogeneous. The short-term stability (<3 h) is better than 1%.

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ELIMINATION OF CHARGING IN THE PROTON-INDUCED X-RAY EMISSION ANALYSIS OF INSULATING SAMPLES

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Anomalous background due to charging in the proton-induced X-ray analysis of insulators is eliminated by inserting a heated carbon filament or by raising the pressure in the sample chamber.

Proton-Induced X-ray Emission (PIXE) has been shown to be a feasible analysing method especially for thin samples^{1,2}). The high sensitivity obtained is partly due to the lower level of the continuous background radiation found in proton bombardment compared with that arising when electrons or photons are used for excitation³⁻⁵). However, when the method is extended to the analysis of samples so thick that they stop the protons, the continuous background radiation is found to increase considerably when the samples are good insulators^{1,3-5}). We have also seen such an effect in thick filters when the protons can pass through. The samples become charged by the proton beam, and, in the discharge, electrons are accelerated producing an intense background of bremsstrahlung which may reach several tens of keV. This bremsstrahlung reduces the sensitivity due both to the higher background level and to the fact that the proton current has to be decreased to adjust for the higher count rate in the detector.

This Letter describes two ways of neutralizing the charge build-up: by inserting a hot filament emitting electrons a short distance in front of the target, as proposed by Shabason et al.⁶), and by increasing the pressure in the target chamber. Both methods avoid the danger of contamination associated with the evaporation of conducting materials on to the sample^{5,7}), or the mixing of target and conducting materials¹⁰).

The filament in the "electron-gun" presented in fig. 1 is taken from a commercial carbon filament bulb. Tungsten filaments were tried but found to contaminate the sample severely when heated. The carbon filament is clamped to two carbon rods. These are fastened to a cylinder of plexiglass so that no heavy elements are heated when the glow current is turned on. A voltage of 7 V, which gave a glow current of 0.25 mA, was sufficient to neutralize the charge from a 50 nA beam of 2 MeV protons. To prevent positive impurity ions

from the carbon filament contaminating the samples, a perforated cap of aluminum kept at +100 V was placed over the filament. The electron-gun was placed in front of the target in an insulated target chamber similar to that described in ref. 11, the batteries being placed outside the chamber at atmospheric pressure. The electric connections were made as shown in fig. 1. The proton current could then be integrated for quantitative determinations without any interference.

Another, simpler, way of neutralizing the charge build-up on thick insulating samples was found to be by increasing the pressure in the target chamber. In

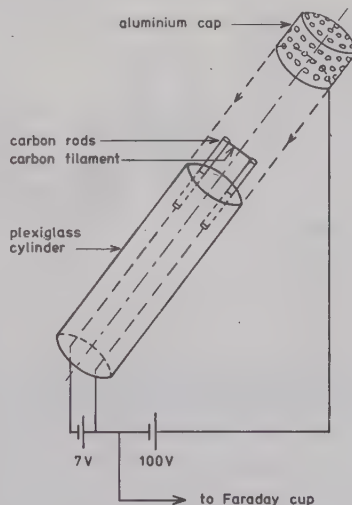


Fig. 1. The electron-gun used to spray the sample with electrons.

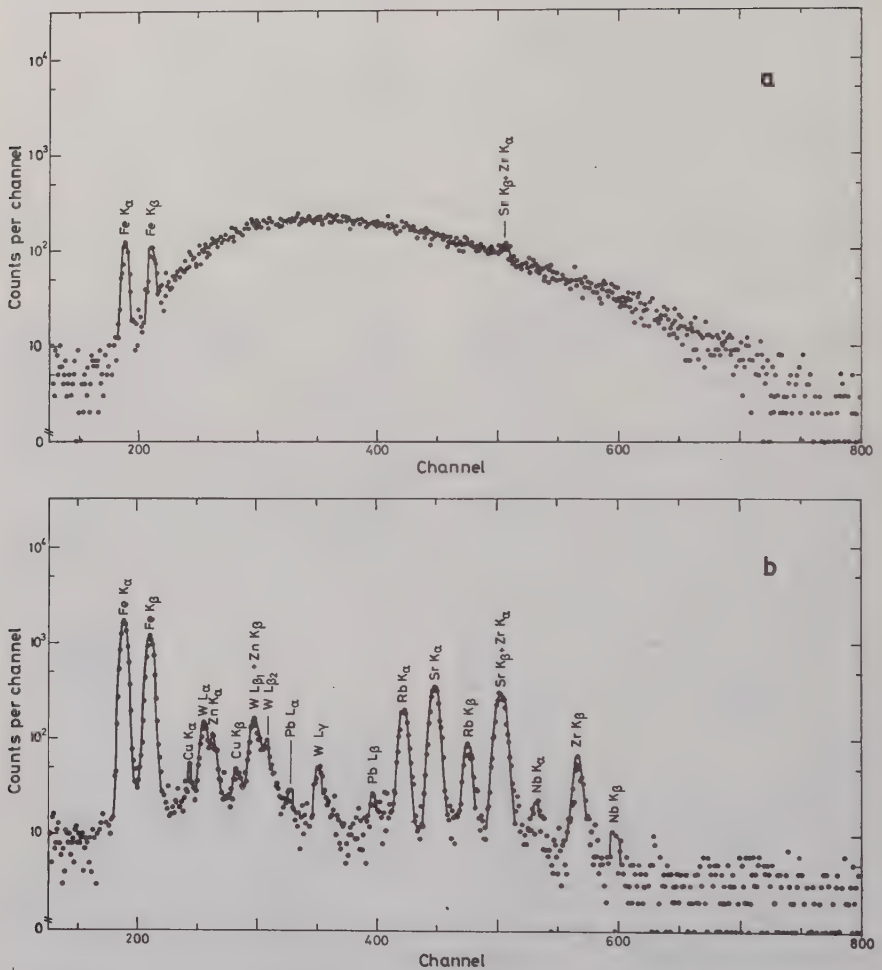


Fig. 2. The spectra from a 3 min analysis of a granite sample with 2 MeV protons, when the low energy X-rays are absorbed in a 280 μ m thick aluminum absorber; (a) when charging limited the proton beam to 3 nA, (b) with a beam current of 50 nA, charging being eliminated by the use of a heated carbon filament in the sample chamber.

ELIMINATION OF CHARGING

the case of 2 MeV protons, the charging ceased when the pressure was raised to at least 1.5 Pa ($\approx 10 \mu\text{m}$). As the X-ray production cross section is a smooth function of proton energy, the slowing down of the protons due to the residual gas in the target chamber and by the very thin carbon layer which grows on the target at low pressure, do not affect quantitative determinations. However, as the residual gas in the target chamber may be a source of impurities, the electron-gun method is to be preferred, when possible.

The drastic decrease in sensitivity due to charging is illustrated in the two spectra shown in fig. 2. Both show a 3 min analysis of a powdered granite sample pressed to a pellet. When the spectrum in fig. 2a was recorded, charging limited the beam current to 3 nA which gave a count rate in the detector varying from 50 to 1000 counts per second. When the electron-gun was turned on, the charging was eliminated and a beam current of 50 nA gave a steady count rate of 400 counts per second, resulting in the spectrum in fig. 2b. The spectrum obtained without the electron-gun but with the pressure in the target chamber raised to 3 Pa ($\approx 20 \mu\text{m}$) was identical with that shown in fig. 2b.

The peaks correspond to 0.9% Fe, 5 ppm Cu, 20 ppm Zn, 40 ppm Rb, 70 ppm Sr, 60 ppm Zr, 5 ppm Nb, 100 ppm W and 5 ppm Pb. When calculating the concentrations, the attenuation of the X-rays and the decrease in X-ray production cross section due to the slowing down of the protons in the sample have been taken into account¹¹).

We have benefitted from discussions with Dr R. Akselsson and Dr T. B. Johansson. We are grateful to Mr K. Sjöberg for building the electron-gun, to Dr Z. Solyom, Dept. of Mineralogy and Petrology, University of Lund, for providing the granite sample and to the Van de Graaff laboratory at the Niels Bohr Institute, Copenhagen, for the possibility of performing this experiment.

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PERFORMANCE OF AN ON-DEMAND BEAM EXCITATION SYSTEM FOR PIXE ANALYSIS

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A system for electrostatic on-demand beam excitation in PIXE analysis has been built and carefully tested. Significantly increased count rate capability without any need for corrections for electronic dead time and with less target deterioration makes the system superior to a traditional system with electronic pile-up rejection. By adding a fast external electronic pulse pile-up rejection system, a pile-up interval of about 250 ns is obtained. The detailed behaviour of the particle beam during deflection and experience from using the system in routine analysis are reported.

1. INTRODUCTION

Particle Induced X-ray Emission, PIXE, was introduced in 1970¹. The method is today used in many laboratories and has been applied to a variety of analytical problems².

For PIXE-analysis, electrostatic accelerators or cyclotrons are normally used to produce charged particles with energy in the interval from 1 to 5 MeV/u. When these particles impinge on a target they create inner shell vacancies in the target atoms. When such a vacancy is refilled the excess energy may be emitted as a characteristic X-ray. The X-rays are normally detected by an energy dispersive Si(Li)-detector with high energy resolution.

Normal beam intensities in PIXE analysis are in the interval from 1 to 200 nA. To reduce the analysing-time, high beam intensity is normally used. The electronics used for detector pulse processing will, however, limit the number of pulses processed per unit time. Too high count rate can cause severe distortion of the pulse-height spectrum. Peak centroid shifts and peak broadening will occur in the spectrum as will pulse pile-up effects. Evaluation of X-ray spectra is normally made by computer codes which are sensitive to spectrum distortions. In addition, the particle beam intensity is restricted by target deterioration, due to dissipation of energy as the charged particles slow down in the matrix. Some samples, e.g. biological tissues, are particularly sensitive to high beam intensities.

2. PILE-UP REDUCTION IN ENERGY DISPERSIVE X-RAY ANALYSIS

2.1. X-ray pulse processing

After detection of an X-ray in the Si(Li) crystal, a pulse proportional to the X-ray energy is delivered from the preamplifier to the main amplifier. A conventional X-ray main amplifier uses pulse shaping time constants of between 2 and 10 μ s, giving pulse processing times in the interval of 20 to 100 μ s. The probability for pulse pile-up effects due to the overlapping of X-ray pulses is proportional to the pulse processing time. In a fictitious X-ray energy spectrum with one single X-ray line, pulse pile-up will appear as a continuum starting just above the full energy peak and ending in a peak at double the energy of the X-ray peak (compare fig.3a). The continuum is due to pulse overlapping when two pulses arrive with a relatively large time difference but still close enough to be added partly in the amplifier. Such a continuum acts as an increased background for other possible peaks in the energy interval in question, thus significantly increasing the lower limit of detection. The discrete pile-up peaks, emanating from pulses very close in time, will interfere with X-ray peaks in their immediate vicinities. Pulse pile-up can be suppressed by the introduction of an electronic pile-up rejector³.

X-ray main amplifiers are more or less sensitive to high count rates which can cause X-ray peak broadening and peak centroid shifts due to incomplete base line restoration. The X-ray spectrum will be distorted by such effects as well as by the pulse pile-up effects. Even very slight changes in the spectrum may introduce gross errors in the quantitative evaluation. The latter is normally made by automatic or semi-automatic computer codes which fit the X-ray spectra. Since computer codes are normally quite sensitive to changes in energy resolution and peak centroid position values, such spectral distortion causes the failure of automatic spectrum evaluation procedures and, since no PIXE laboratory running on a routine basis can avoid the use of computer evaluation of X-ray spectra, there is an obvious need for suppressing them.

2.3. Electronic pile-up rejector

The electronic pulse pile-up rejector (PPR) includes a fast amplifier parallel to the slow, high-resolution spectroscopy amplifier. The PPR senses if two consecutive events from the preamplifier overlap in time, normally with a pulse pair resolution of 0.5 to 1 μ s. If two events overlap, both are rejected by inhibiting the main amplifier output, thus almost completely eliminating the

pile-up continuum. To enable a quantitative analysis, the electronic deadtime thus introduced has to be corrected for.

The discriminator of the PPR is set at a threshold level, small enough to include the pile-up emanating from X-rays of the lowest energy of interest. Noise, however, should not trigger the PPR since this would introduce unnecessary electronic dead-time.

The time interval in which pulse pile-up due to the finite time resolution of the electronics cannot be detected is called the pile-up interval τ . Any two pulses which arrive within this interval are not rejected by the PPR and occur as one peak at an energy approximately equal to sum of the two X-ray energies referring to the two pulses. Knowing the number of pile-up events per unit time, τ can be derived from Poisson statistics³ giving the expression :

$N_{ij} = (\tau_{ij} + \tau_{ji}) \cdot N_i \cdot N_j$, $i \neq j$ (A), where N_i is the number of events with energy E_i per unit live time, N_{ij} the number of pile-up events emanating from the combination of E_i - and E_j - events per unit live time and τ_{ij} the pile-up interval between pulses from X-rays of energy E_i and E_j . For double energy peaks ($E_{ii} = E_i + E_i$) this expression becomes:

$N_{ii} = \tau_{ii} \cdot N^2$ (B). The formulae show that the number of pile-up events will increase as the square of the count rate. For very high count rates there will also be a significant probability for triple pile-up (compare fig.3b).

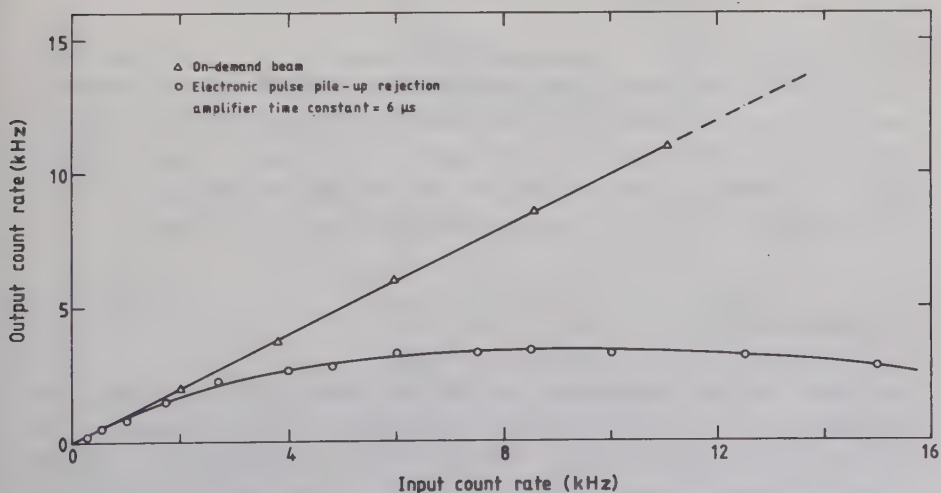


Fig 1. Effective count rate (counts per unit real time) in the X-ray spectrum versus the input count rate for on-demand beam irradiation (Δ) and electronic pile-up rejection ($\circ$) respectively. The results were obtained during irradiation of a thick copper plate.

With an electronic PPR, an increased input count rate does not always imply an increased output rate. Instead, a maximum output count rate, determined by the pulse shaping time constant, will be reached for a certain input count rate (fig.1). If the count rate is high enough, the deadtime will eventually reach 100% and no output will occur from the amplifier. The system is paralyzed.

2.3. Pile-up reduction by on-demand beam excitation

A different technique of pulse pile-up reduction makes use of an on-demand excitation system^{4,5}. When an event is detected at the output of the preamplifier, the excitation source is shut off. The source is then kept off during the pulse processing time. When the amplifier is ready to accept and to process another pulse the excitation source is turned on again. In this way a non-paralyzable system is obtained.

In particle induced X-ray analysis a suitable way to shut off the excitation source is by the insertion of two parallel electrostatic deflection plates in the beam transport tube⁵, between which the charged particles pass on their way towards the sample. When an X-ray event has been detected, a transversal electrical field is applied between the plates forcing the charged particles to deflect and thus removing the particle beam from the sample. The electric field is switched off once the event has been processed in the amplifier.

If a system for fast leading edge discrimination is used to detect the X-ray signal from the preamplifier the beam may be turned off within a very short time. The pulse pile-up interval is determined by the sum of the times for the leading edge discriminator to detect the pulse, for the signal to reach the beam deflection circuit, to deflect the beam and the transit time for the last undeflected particles to move from the deflection plates to the target.

3. ON-DEMAND BEAM SYSTEM

An on-demand beam excitation system has been implemented in the beam line of the PIXE-facility at the Lund Institute of Technology⁶. The electronics of the system is similar to the one presented in ref.⁵ which is referred to for details of electronic design. However, the discharge time of the deflection plates is shorter in the system discussed here.

3.1. Technical description

A pair of deflection plates (0.46 m x 0.04 m) made of aluminium are mounted in parallel with a spacing of 8 mm, in one of our standard beam transport tubes (diam.:0.06 m). The distance between the centre of the beam deflection system and the target is 1.0 m. A beam collimator (diam.:3 mm) is placed 0.6 m from the target. When deflected, the beam hits the collimator and no particles reach the sample.

The deflection is controlled by the X-ray signals from the preamplifier (see fig.2). This is a pulsed optical feedback preamplifier (Kevex 2003) producing step signals proportional to the X-ray energies detected, thus forming an increasing ramp voltage signal. When the DC-level reaches +5V the preamplifier is reset by an optical signal from a light emitting diode. An emitter follower stage, necessary to match impedances, differentiates the preamplifier signal, which is then amplified by a fast timing filter amplifier (ORTEC 474) and fed into a single channel analyzer (ORTEC 406A), the output signal of which (LLD output, +5V, 500 ns wide) triggers the control electronics (TU) of the deflection system. The control electronics provides a 95 V positive going pulse to open a power tube (PL 519) for the grounding of one of the deflector plates. These plates are normally both maintained at a voltage of 1–2 kV. The 10% to 90% rise time of the electric field between the plates from zero to 1200 V/cm is 35 ns.

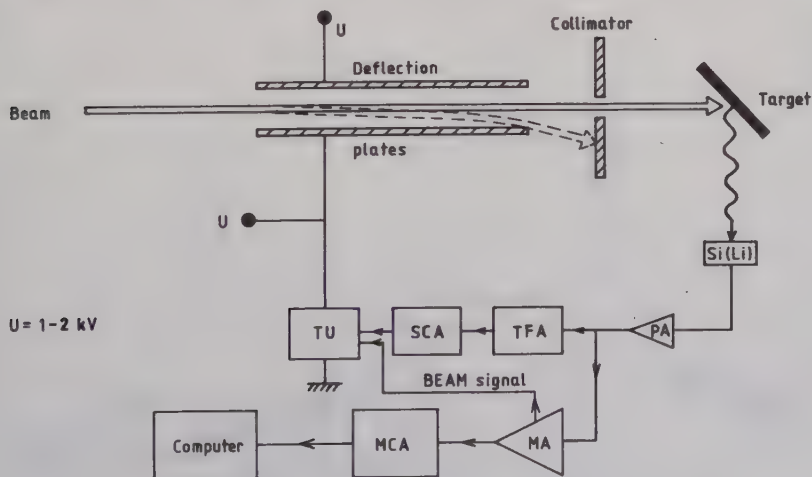


Fig 2. Block diagram of the electronics used for on-demand beam pulsing. PA = preamplifier, MA = main amplifier, MCA = multi-channel analyser, TFA = timing filter amplifier, SCA = single channel analyser, TU = trigger unit and BEAM signal = logical output from main amplifier during the processing of a pulse.

The deflection duration can be set on the control electronics or be controlled by the BEAM-signal from the amplifier. This signal shows that the amplifier is busy processing an event and the deflection is maintained also during the long busy intervals (0.5–2 μ s) following a pulsed optical reset in the preamplifier.

3.2. Pile-up interval

During the detection of an X-ray event, the charge collection time in the Si(Li)-detector is typically around 50 ns³. The measured delay of the signal during its transmission from the preamplifier to the power tube is about 300 ns. For the projectiles normally used in this laboratory (protons, 2.55 MeV), the transit time from the plates to the target is about 40 ns. When bombarding a thick homogeneous Cu-plate with different count rates (1500–5000 cps) the double energy pile-up peak for the K_{α} -line has been measured and from formula (B) has been calculated to be 400 ± 20 ns ($\pm$ one standard error of the mean). This is in fair agreement with the measured time delays. In fig 3 are shown the spectra from bombarding this target with a) no PPR, b) with PPR, c) with on-demand beam irradiation and d) with simultaneous use of PPR and on-demand beam irradiation respectively (the total effective count rate in each spectrum is about 4500 cps).

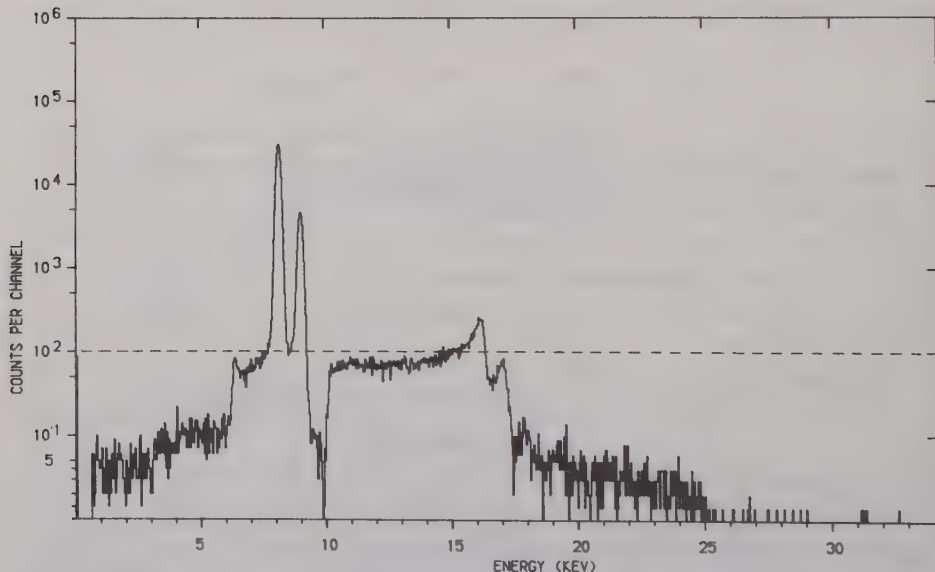


Fig 3. The spectra obtained during equally long bombardments of a thick copper plate using a 340 μ m Mylar X-ray absorber and a amplifier time constant of 4 μ s. The effective total count rates are in all cases about 4500 cps (real time). The broken lines shown at 100 counts per channel are given to facilitate comparison between spectra. The spectra refer to the following conditions: a) no pile-up rejection

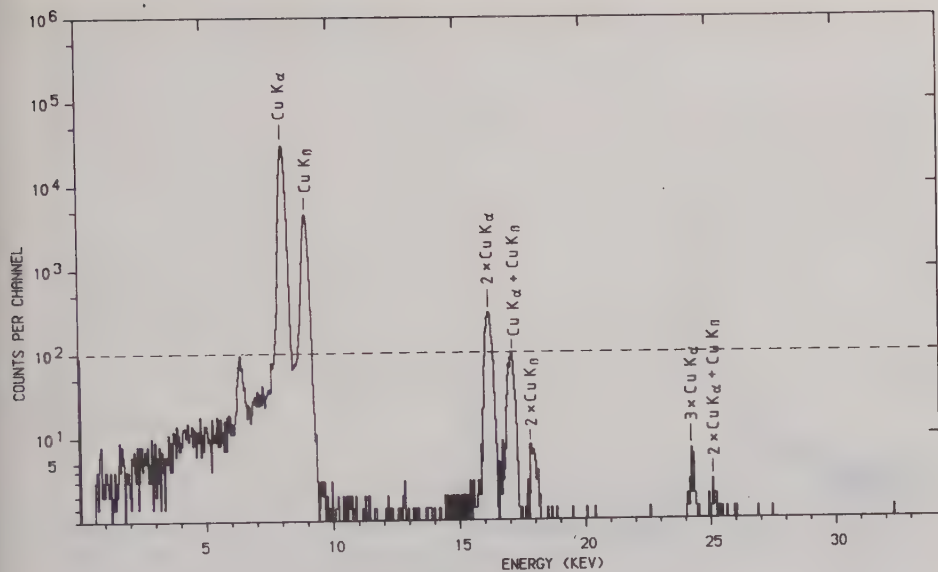


Fig 3 b) electronic pulse pile-up rejection

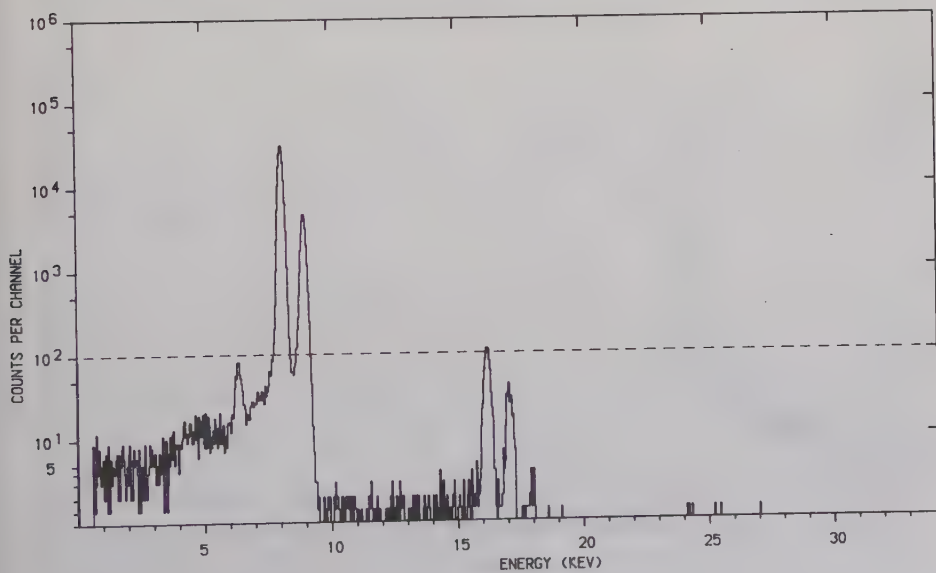


Fig 3 c) on-demand beam irradiation

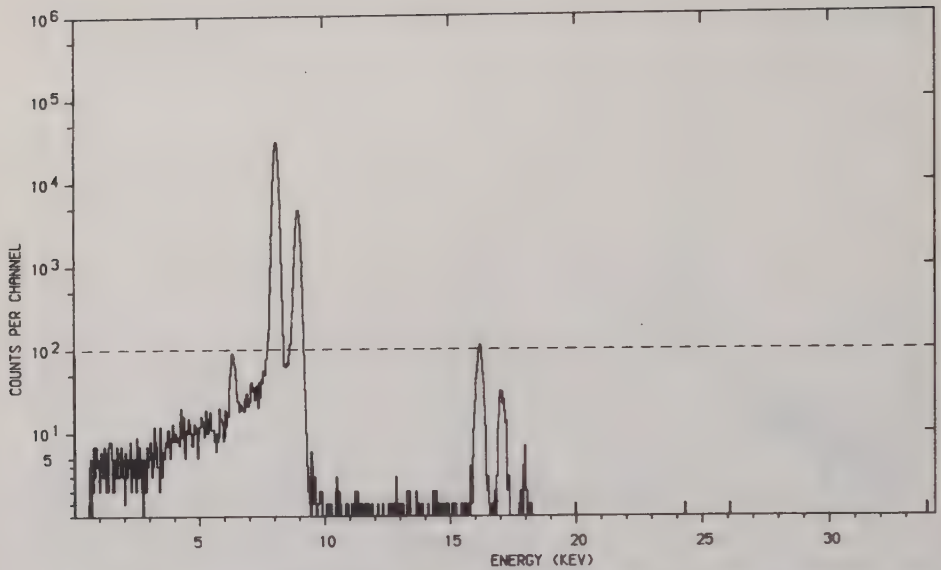


Fig 3 d) the simultaneous use of on-demand beam irradiation and electronic pile-up rejection

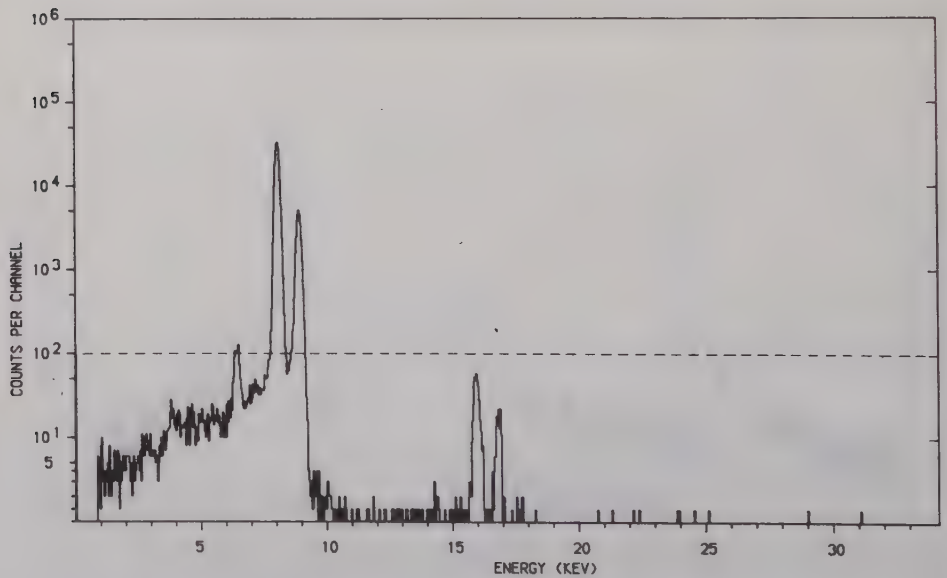


Fig 3 e) similar to d) with addition of a fast external PPR.

In fig. 3 b), a drastic suppression of the continuous pulse pile-up can be observed with an electronic PPR as compared to fig. 3 a). In c) the use of on-demand irradiation is superior to PPR in reducing double pile-up peaks and in that no triple pile-up peaks are observed. The simultaneous use of on-demand irradiation and PPR (fig. 3 d) gives a slightly lower pile-up continuum than in c). If no PPR is used when the beam is deflected during the processing of an X-ray event and hence no electronic inspection is performed, another event, e.g. caused by particles being scattered out of the deflected beam into the normal beam path and thus reaching the sample, can be registered during the off-beam period thus interfering with the event being processed and causing pile-up in the continuum region. In the analytical set-up reported, the commercially available PPR in the X-ray main amplifier is used together with on-demand beam irradiation.

It is possible to shorten the pile-up interval in on-demand beam irradiation if commercial modules with smaller signal delays are used for leading edge discrimination and by reducing the signal delay in the control electronics (TU in fig. 2). We estimate that in this way it would be possible with this on-demand beam system to reach a pile-up interval of about 200 ns.

For protons with energies in the interval of 1 to 4 MeV and for alpha particles from 3 to 9 MeV, the variation in the pile-up interval will be less than 10%, which is insignificant for practical analytical purposes.

In commercial PPR:s the manufacturers, due to the need to compromise between detecting pulse pile-up from low energy X-rays and suppression of electronic noise⁷, limit the pulse pair resolution to about 500 to 1000 ns. It is, however, possible to obtain a pulse pair resolution of less than 300 ns by using commercial NIM modules.

In fig 4 is shown a block diagram of the electronics which have been used for external pulse pile-up rejection. A time-to-pulse-height-converter (TPHC, Ortec 467) has been used to measure the time intervals between successive X-ray events and if two events occur within a preset time interval (TPHC time interval), a pulse will be produced and the TPHC is then ready for a new measurement. The negative signals delivered from the fast discriminator (FD) upon the detection of an X-ray event are used to stop and with a delay (10 ns) to start the TPHC. A +8V standard pulse (SCA in fig 4) with a width of 10 μ s is produced as soon as a time interval has been measured and, after a suitable delay, it may be used to

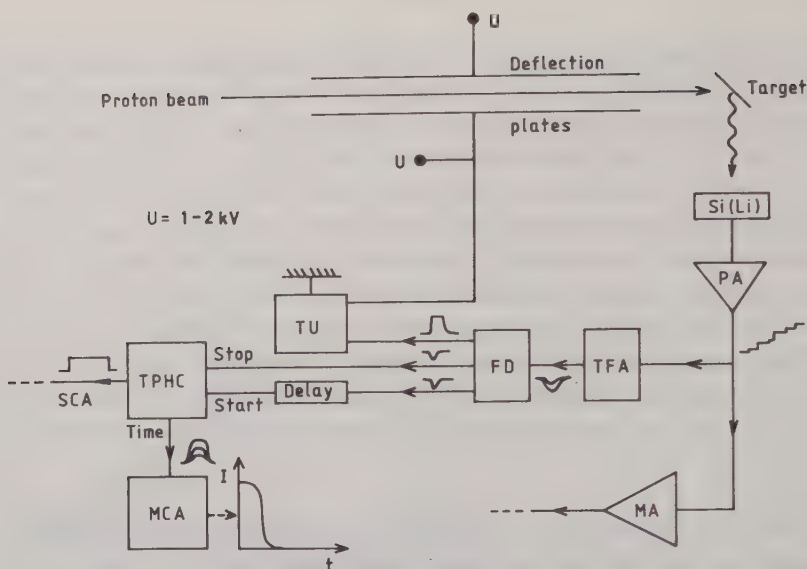


Fig 4. Block diagram of the electronics used for external pile-up rejection and when studying the detailed behaviour of the proton beam. A target is irradiated and the preamplifier signals enter a timing filter amplifier (TFA) followed by a fast discriminator (FD). The latter triggers the trigger unit (TU) and supplies a time-to-pulse-height-converter (TPHC) with both start (with a suitable delay) and stop signals.

inhibit the input of the ADC thereby rejecting the X-ray events which would otherwise be found as pile-up in the spectrum. If a TPHC interval of $2 \mu\text{s}$ is chosen ideally all pulses less than $2 \mu\text{s}$ from one another will be rejected. In this way a pile-up interval of about 250 ns is obtained. The ultimate limit of such an electronic rejection system, able to distinguish between two adjacent pulses, will be set by the charge collection time in the Si(Li) crystal (see sect. 3.2) and the pulse pair resolution of the electronics. The rise time of the X-ray pulses from the preamplifier has been measured to be about 100 ns . Used together with an on-demand beam system it is then possible to achieve a reduction of the intensity of the double energy peaks as compared to pure on-demand beam irradiation without introducing any significant dead-time ($< 1\%$). In fig 3e is shown a spectrum similar to 3d but with the addition of the electronic pulse pile-up rejection system described.

To account for the remaining pile-up peaks, which will still be significant at high count rates, the spectrum evaluation computer code in use has been modified to facilitate accurate corrections for pile-up peaks .

3.3. Routine applications

The on-demand beam system described is in routine used and works very well requiring only minor maintenance. The practical count rate is limited to about 10 000 cps (with an amplifier time constant of 6 μ s), primarily by the limited power capacity of the deflection tube. This is a common electron beam deflection tube used in many commercial colour television sets and thus readily available at a low cost. It could, however, be replaced by other types of tubes capable of withstanding much higher power dissipations, e.g. high power transmitting tubes.

3.4. Performance of the on-demand beam system

Extensive work has been carried out to test the behaviour of the deflection system in detail and to check whether it is reliable in conjunction with quantitative PIXE-analysis. The tests normally described in the literature^{5,9}, imply the comparison of X-ray spectra with electronic pile-up rejection with those obtained with an on-demand beam system (fig.3). It is, however, also important to study the detailed behaviour of the particle beam during deflection and return.

3.4.1. Deflection and return of the beam

When an X-ray event is detected, the signal is sensed by the on-demand electronics. A pulse then opens the power tube to ground one of the deflection plates and thus deflect the beam. The removal of the beam from the target should occur as rapidly as possible. Similarly to many other laboratories, in the Lund PIXE arrangement we use a diffuser foil (1 mg/cm² gold foil) to obtain a homogeneous beam at the target⁶. The foil scatters the particles in the beam away from their initial directions. When deflection takes place, the beam is moving transversally and the particles will eventually hit the collimator situated just in front of the gold foil. Due to the scattering in the collimator edges and the foil, some particles may hit the sample and produce X-rays during and after the beam removal. If these X-rays reach the detector, they cause pulse pile-up in the electronics.

To study the detailed performance of the system the TPHC (see fig. 4) has been used to measure the time interval between two successive X-ray events when the beam deflection is active. In addition to the +8V pulse (see sect. 3.2) an analogue signal with an amplitude proportional to the measured time interval is produced subsequent to each time measurement. The TPHC is started by an X-ray signal after a suitable time delay and stopped by the successive X-ray signal. By selecting the delay of the start signal properly (about 250 ns), it is possible to start the time measurement just before the deflection of the beam starts. As the deflection proceeds, the probability for the occurrence of a new event will decrease. Hence, with repeated beam deflections, the frequency of stop signals from a successive event is expected to decrease with the time after beam removal. This can be demonstrated by storing the measured time intervals as a time spectrum in a multichannel analyser.

Figure 5 shows a time spectrum obtained during a 10 min irradiation of a Cu-target with a deflection frequency of about 5 kHz. The TPHC time interval is set to 0.4 μ s in the left-hand part of fig.5 and to 80 μ s in the right-hand. The diagram shows the time dependence of the count-rate when the deflection takes place. The 90% to 10% fall time is about 25 ns. The right-hand part of the figure shows the behaviour of the beam when the deflection duration is set on the control electronics to 65 μ s. The beam returns to the target within 64 μ s and the beam intensity then recovers with a 10% to 90 % rise time of 2.1 μ s. The longer time for beam return is due to the longer time required to return the grounded plate to its initial potential than to perform a sudden grounding.

3.4.2. Beam charge integration

Since the time required to remove the beam from the target is very short compared to the pulse processing time ($<1\%$), no dead-time corrections have to be made. However, the deflection system (power tube, plates, etc) will act as a strong source of electromagnetic radiation in the radiofrequency band. The current measurement system, including irradiation chamber, coaxial cables and Faraday cup, forms an antenna, picking up the radiation. The currents which may be induced (normally below a few nA) can cause significant inaccuracies when low beam currents ($I < 10$ nA) are used. The rather large irradiation chamber used in this particular experimental arrangement may be part of the explanation of this phenomenon. Careful shielding and grounding eliminate or suppress these currents but the attention of presumptive users of such systems should be drawn to the

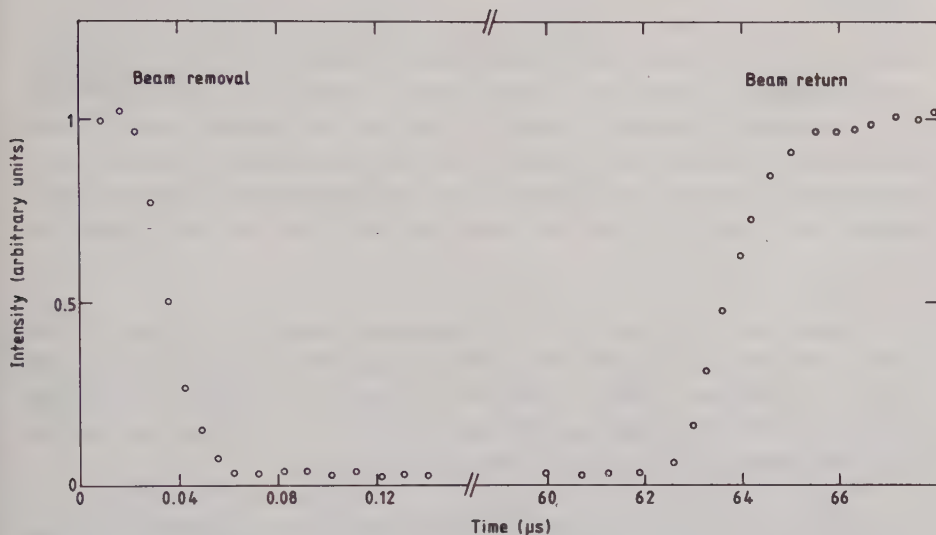


Fig 5. Time spectra from a TPHC with TPHC time interval of 400 ns (left) and of 80 μ s (right) obtained during the irradiation of a thick copper plate with a deflection frequency (cps) of about 5 kHz.

problem, in order to avoid analytical inaccuracies when low beam currents are used.

The use of a collimator to stop the deflected beam requires careful alignment of the beam, i.e. the beam must pass straight through the collimator when no deflection takes place. If the main part of the beam hits one side of the collimator but part of the beam is still let through the central hole, it will hit the sample and produce X-rays thus triggering the beam deflection. During the pulse processing, when no particles are expected to reach the sample, part of the beam is steered into the collimator hole, thus giving a residual beam intensity at the sample and causing pulse pile-up and erroneous charge integration. This situation may be detected by repeated analyses of a well-known reference standard sample¹⁰ and can be avoided by careful initial alignment of the particle beam through the collimator.

4 SUMMARY

Compared to the electronic PPR, an on-demand pile-up reduction system has several advantages. Since the excitation source is shut off almost immediately after an event is detected, there is no need for any dead-time corrections in quantitative analysis and the system cannot be paralyzed. Compared to a conventional PPR, the pile-up peaks in the X-ray spectrum will be significantly reduced for the same effective count rate (cps, real time) as can be seen from fig.3.

Furthermore, since the output rate of an on-demand system will be equal to the input rate (see fig.1), fewer count rate problems will occur. High output count rates can be achieved without the occurrence of any significant peak centroid shifts or peak broadening since the amplifier will be able to perform adequate base-line restoration for each individual event.

Target deterioration due to heating is dependent on beam intensity and deterioration due to radiation damage proportional to the total integrated beam charge (accumulated radiation dose). Being without any dead-time losses, the on-demand pulsed beam excitation system enables the use of lower currents and less charge for the same amount of information. For samples which are sensitive to radiation damage or heating, e.g. biological samples or samples containing volatile compounds, the use of on-demand beam excitation shall prove especially advantageous.

A detailed study of the deflection process shows that the beam intensity falls off very rapidly as soon as the control signal reaches the electronic tube which grounds the one plate and also recovers acceptably quickly when the high voltage is reapplied to the plate. The total delay of signals from detection of X-ray events in the detector crystal to turn-on of the triggering unit, which grounds the plate is about 300 ns in our experimental arrangement but can be further improved by selecting electronics with shorter pulse delays.

A fast external pulse pile-up rejector was designed using standard NIM modules and, with the combined use of the on-demand beam excitation and the external PPR a pile-up interval of about 250 ns has been obtained.

It is our experience that minor problems may arise in the use of on-demand beam electronics since extra currents can be induced in the charge measurement system

(especially for large volume chambers). These problems can, however, be overcome by careful shielding and grounding. To avoid increased pile-up and inaccuracies in quantitative determinations, careful alignment of the particle beam is recommended.

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CHARACTERISTICS OF WELDING FUMES

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ABSTRACT

The aerosols from 13 common electric arc welding processes have been characterized regarding total mass emission, particle size distribution, elemental composition and, when applicable, the oxidation state of chromium. The characterizations have been performed systematically for different combinations of welding current and welding voltage.

INTRODUCTION

In the work environment electric arc welding is a common process producing complex and abundant fumes. Since the distribution in size and elemental composition of the produced particles also vary within wide limits for different modes of operation, the finding of dose-response relations, the design of effective monitoring programmes and the choice of strategies for elimination techniques constitute a challenging task for industrial hygienists, epidemiologists, toxicologists, etc.. A fundamental prerequisite for the successful tackling of these central tasks is a thorough knowledge of the size distribution and composition of the welding aerosol particles. Although not dealt with explicitly in this work, in this connection other environmental factors, e.g. gaseous emissions, electromagnetic radiations and ergonomic aspects are of the outmost concern.

In a recent book, Moreton and Falla¹ have summarized existing information in the field of analysis and sampling of welding fumes while in a volume from the American Welding Society² the results of a major study of fumes and gases in the

the welding environment are reported. It is well known from other studies of welding aerosols that variations in current and voltage can influence the characteristics of the welding fumes produced^{3,4,5}.

To verify and extend existing information on welding aerosols, a comprehensive investigation of the total mass emission, particle size distribution, elemental composition and, when applicable, the oxidation state of chromium has been performed for 13 different welding methods (Table 1). The methods were chosen in cooperation with representatives of manufacturers and other experts on welding techniques and cover the three main types of welding: Shielded Metal Arc Welding (SMAW), Gas Metal Arc Welding (GMAW) and Gas Tungsten Arc Welding (GTAW). Most methods have been chosen from a Swedish firm manufacturing welding material, ESAB, which has an extensive export to the world market. In Table 1 the corresponding AWS classifications are, when possible, given.

Electrode	Type	Coating	AWS ^{a)} -class.	Diam. (mm)	Gas
1 OK 38.65	SMAW	iron powder, low hydr. zirconium added	E 7028	3.25	-
2 OK 38.85	SMAW	iron powder, low hydr.- rutile	E 7028	5	-
3 OK 38.95	SMAW	iron powder, low hydr. zirconium added	E 7028	4	-
4 OK 48.00	SMAW	iron powder, low hydr.	E 7018	2,3.25,4	-
5 OK 61.41	SMAW ^{b)}	rutile	E 308 L-15	3.25	-
6 OK 63.35	SMAW ^{b)}	low hydrogen	E 316-15	2.5,3.25,4,5	-
7 OK 69.21	SMAW ^{b)}	low hydrogen-rutile	-	3.25,4,5	-
8 OK 12.51	GMAW	-	E 70 S-6	1.2	CO ₂
9 OK 16.32	GMAW ^{b)}	-	ER 316 I Si	1.2	Ar
10 OK 16.32	GMAW ^{b)}	-	ER 316 I Si	1.2	Ar/CO ₂
11 OK 18.01	GMAW ^{c)}	-	ER 1260	1.2	Ar
12 OK 18.13	GMAW ^{c)}	-	ER 5154	1.2	Ar
13 Tungsten Th added	GTAW ^{b)}	-	-	-	Ar

a) AWS-class. = American Welding Society classification.

b) welding on stainless steel; c) welding on aluminium.

Table 1. A list of the welding methods included in this study. The numbers are used for identification in the various figures.

Since size distributions and elemental compositions have been investigated for several sets of current and voltage for each of the 13 methods of welding studied, an extensive database has been created. In this paper the results are summarized. A complete listing of the results can be obtained from the authors⁶.

MATERIAL AND METHODS

SAMPLING EQUIPMENT

Figure 1 shows the design of the sampling arrangement. The welding takes place beneath an aluminium hood. Two fans (ESAB, OFA, 13 kPa at 60 m³/h) connected in series pull air through a glass fibre filter (Millipore AP, 2529325, diam: 293 mm) on top of a pipe connected to the hood, in which the welding fume is collected. This equipment allows reproducible and representative sampling of fume from manual and automatic welding processes. The low velocity of the air around the welding point (< 0.15 m/s) assures that the sampling procedure has no significant impact on the welding process and aerosol formation.

The total mass of welding aerosol is determined by gravimetric analysis of the glass fibre filters. These are insensitive to relative humidity and static electricity and hence repeated weighing over periods of several weeks give variations well below 0.1 % of the filter weight. For the collections in this study, the uncertainty in the total mass determinations is, in all cases, below 5%.

During the welding of a rod the filter will gradually clog and the pressure drop over the filter increase. The air flow then decreases and limits the amount of fume which can be collected on one filter. Tests have demonstrated the sampling efficiency to be above 95% for the collection of 1000 mg of welding fumes (fig. 2), which is quite sufficient for the sampling situations in the present study.

Due to diffusion, minor losses of small particles to the walls of the sampling equipment occurred. After a large number of collections (≈ 100) the pipe and hood were washed with distilled water and the water filtered. The filters and filtrates were analysed for iron (PIXE analysis). A comparison between the mass of airborne iron produced and the mass deposited on the walls indicates that losses from the wall are less than one per cent of the total mass of fume produced. In this determination, large globular metal spatter has not been considered.

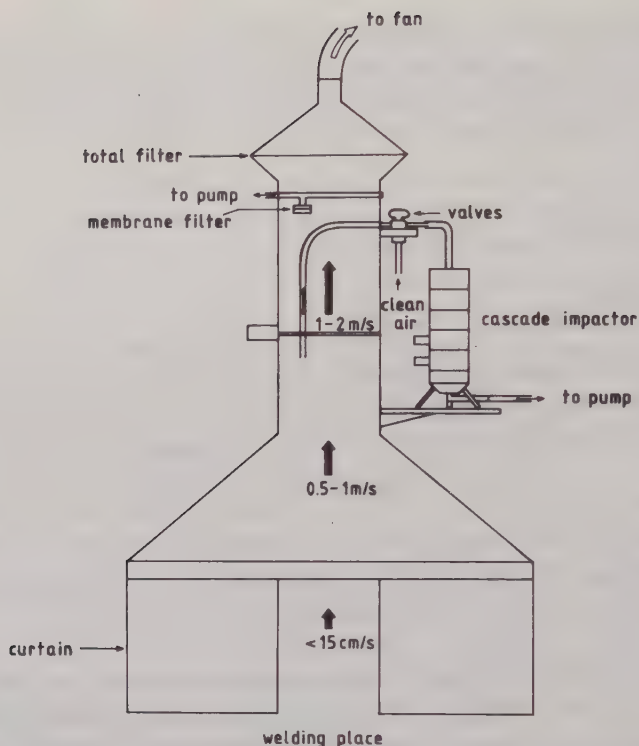


Figure 1. Sampling equipments for the characterization of welding aerosols. The arrows indicate the air velocity in different parts of the system.

The glass fibre filters are not well suited for chemical analysis since they contain high concentrations of impurities. Hence membrane filters made of mixed esters of cellulose (Millipore HAWP, diam.: 37 mm, pore diam.: $0.45\ \mu\text{m}$) have been used for determining the elemental composition of the aerosol. These filters contain insignificant concentrations of the elements of interest. A small portion of the total aerosol ($< 0.5\%$) is collected on the membrane filter for subsequent elemental analysis. To check for possible variations due to the filter orientation, three filters were placed in different positions inside the pipe facing the air stream. While welding, sampling was performed simultaneously with all three filters and the relative elemental composition was determined for each of them. The compositions of the three samples agreed well within 5%. Since the filter efficiency is approximately 100% for all particle sizes⁷, the samples collected should be representative of the welding aerosol. However, due to the difference between the face velocity through the filter and the velocity in the tube, too many large particles will be collected from the aerosol. According to formulae given by Davies⁸, the oversampling of particles with an aerodynamic

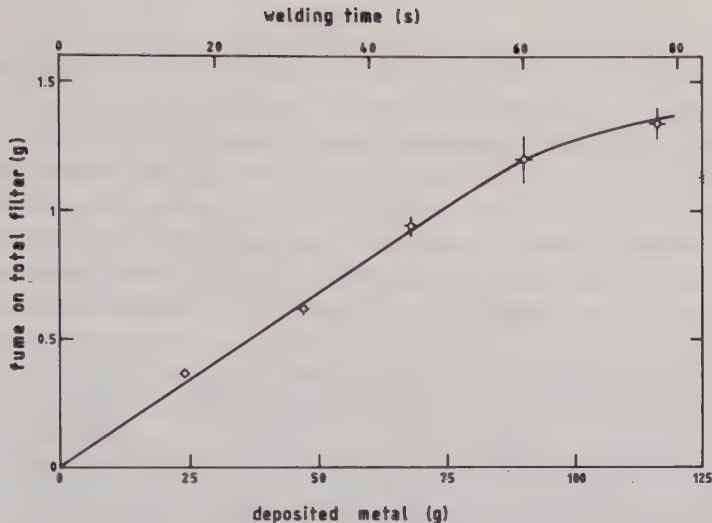


Figure 2. Performance of total fume sampling. Welding was performed with coated electrodes (OK 48.00) with a core diameter of 6 mm and a welding current of 300 A DC, reversed polarity. The error bars show one standard error of the mean.

diameter of less than $5\text{ }\mu\text{m}$ will be less than 10% and in previous studies^{3,9} it has been shown that welding aerosols contain very few large particles (more than 95% of the mass represents particles with aerodynamic diameters less than $1\text{ }\mu\text{m}$)

Since the membrane filter is used only for determining chemical composition, oversampling of certain fractions of particle sizes will only be important if different particle sizes have different compositions.

To determine the particle size distribution, a probe was inserted into the pipe facing the air stream to collect a small sample of the welding aerosol into a Battelle-type cascade impactor¹⁰ placed outside the pipe wall. The nominal air-flow of this single orifice impactor was 1 litre/minute. The diameter of the probe was only 4 mm and to secure representative sampling, the sampling probe was allowed to move in a spiral back and forth over the entire cross section of the pipe. Several spirals were completed within a sampling period (30-60 seconds).

Since very dense aerosols are produced during welding and since the particle sizes which deposit on the two last stages in the impactor are predominant, the welding aerosol was diluted (1:10) by clean air (air drawn from outside the

building) before entering the impactor. Consequently the air velocity in the sampling tube from the probe will be low and diffusion losses of small particles will occur as will, sedimentation losses of large particles in the horizontal part of the tubing. These losses have been calculated¹¹ and are shown in fig.3. Since Reynolds number (Re) was about 50, i.e. well below the limit for turbulent flow ($Re \approx 2300$), the losses have been calculated assuming laminar flow with no turbulent mixing. Although by restricting sampling to an interval of from about 0.01 to 3 μm these losses represent limiting factors, as was mentioned above, these particle sizes constitute more than 95% of the mass of the welding aerosols.

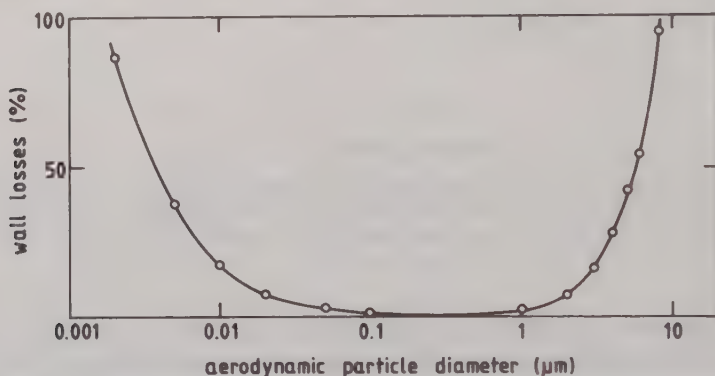


Figure 3. Calculated wall losses in the impactor tubing plotted versus particle diameter¹¹.

Similarly to the membrane filter the impactor probe samples subsokinetically. However, the oversampling (which occurs for particles with aerodynamic diameters larger than 5 μm), is insignificant since because of sedimentation any such particle, will not be able to penetrate the impactor tubing (see fig.3). Although the aerosol was diluted, for reasonable sampling times, some risks of overloading will still remain. Since even a slight overloading of the collection plates can severely alter the collection characteristics of a stage, further improvements have been carried out. By rotating the impaction plates off-axis during sampling, the particles are made to deposit over a larger area (30-60 times larger). This results in a significant improvement in collection performance and also facilitates accurate PIXE-analysis. Further details of this impactor modification are given in ref.¹².

ANALYTICAL METHODS

A brief description of the analytical procedures will be given here, but for a more detailed discussion see refs.¹²⁻¹⁵.

The elemental composition of the welding aerosol samples collected has been determined mainly with the multielemental analytical method Particle Induced X-Ray Emission analysis, PIXE¹². We have used protons (with an energy of 2.55 MeV) from an electrostatic accelerator to irradiate a sample (normal irradiation time 1-5 min). Vacancies are created in the inner shells of the atoms in the sample. When these vacancies are refilled, X-rays with energies characteristic of the atom from which they originate are emitted. Measuring these X-rays with a semiconductor detector (Si(Li), sensitive area = 10 mm², FWHM = 160 eV at 5.9 keV) in combination with suitable electronics will yield simultaneous quantitative results for all elements heavier than about phosphorous, with detection limits of the order of nanograms (1 ng = 10⁻⁹ g). In fig.4 is shown an example of a typical X-ray spectrum from the irradiation of a sample of welding fumes.

For the analysis of one important light element, fluorine, we detect simultaneously the gamma rays produced in the nuclear reaction $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ using a large volume sodium iodide crystal (detection limit 100 ng)¹⁶. Thin fluoride targets of known thicknesses are used as standards for quantitative analysis.

Since in this investigation, more than 3000 multielemental analyses had to be performed, access to the PIXE method with nuclear complementary techniques was a necessary condition for its realization. However, only the elemental composition is determined by the PIXE-method. Since in the case of chromium the oxidation state and probably also the solubility¹⁷ are of major importance in evaluating health hazards, a special analytical procedure¹⁵ was developed to quantify the masses of soluble and less soluble Cr(III) and Cr(VI). This procedure includes PIXE-analysis and complementary techniques such as Electron Spectroscopy for Chemical Analysis, ESCA¹⁸, a spectrophotometric method, DPC¹⁹ and transmission electron microscopy (TEM).

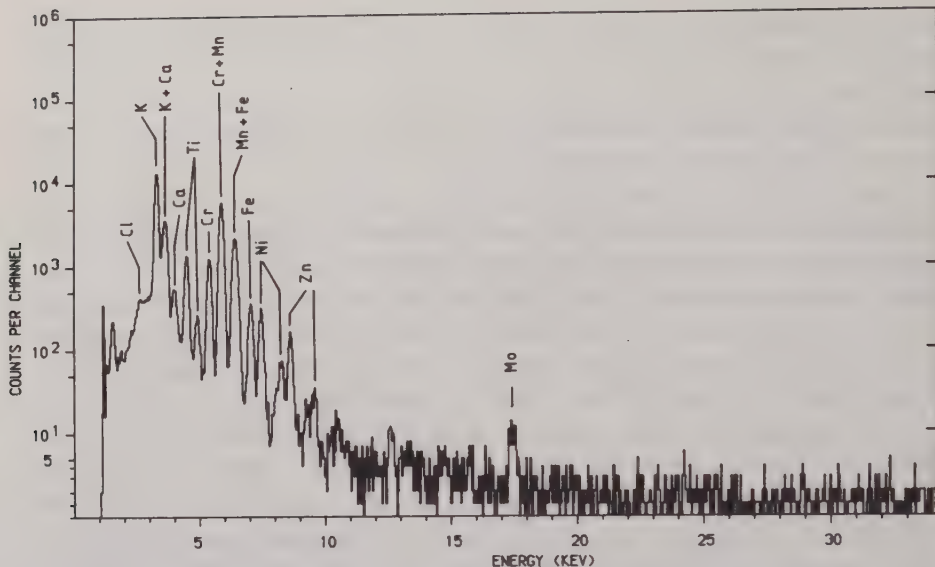


Figure 4. X-ray spectrum from the PIXE analysis of a welding fume sample (OK 69.21, I=140 A, U= 22 V) collected during stainless steel welding.

EXPERIMENTAL PROCEDURE

ANALYTICAL PROCEDURES

To determine the total masses of aerosols the pre-weighed glass fibre filters were re-weighed as soon as possible after collection. They were compared with pre-weighed blank filters to correct for possible systematic changes in filter weight. After weighing, a piece ($3 \times 3 \text{ cm}^2$) was punched from the filter and then transferred to a sample holder (a $5 \times 5 \text{ cm}^2$ slide frame). The samples were analysed by PIXE for about 60 seconds to determine the iron content per unit area of the filter. From this the total mass of iron on the filter can be determined and by comparison with the total mass of aerosol, as determined by weighing, the relative iron content can be calculated. Except in the case aluminium welds, the iron concentration was then used as a reference for determining the elemental composition on the membrane filters.

By scanning the filter area with a proton beam, the homogeneity of the aerosol deposit on the filter surface has been determined to be better than 3%. Since sample thicknesses may sometimes exceed 1 mg/cm^2 , corrections for proton slowing-down and X-ray attenuation in the sample have been made. Taking this into account, the accuracy of the iron determination is typically 5%.

The membrane filters were weighed before and after sampling (using a Sartorius microbalance with a stated standard deviation of $1\text{ }\mu\text{g}$). These filters were very sensitive to changes in relative humidity and to electrostatic build-up, although blank reference filters were used to correct for systematic weight changes due to the absorption of water and an α -emitting radioactive source and a piezo-electric decharger to reduce the effects of static electricity. Consequently, the gravimetric analyses were not sufficiently reliable for total aerosol mass determinations (the accuracy was in the interval from 10 to 30 %). The results were, however, used to double check the glass fibre filter determinations. After weighing, the filter was cut into two pieces one of which is glued to an aluminium frame which was mounted in a standard slide mount for PIXE analysis. The other half of the filter was stored in a Petri tray as a reserve sample. The sample was irradiated for 100 to 300 seconds with a proton current in the range from 5 to 50 nA using a proton beam area of 0.5 cm^2 . The masses of all elements heavier than sulphur were determined and during the proton irradiation the 6 to 7 MeV gamma-rays from the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$ reaction were detected with a $5\times 4''$ NaI-crystal and counted for determining the fluorine content. While only 0.5 cm^2 of the total filter area was analysed during PIXE analysis, according to PIXE-measurements the aerosol deposit on the membrane filter was homogeneous within 2%, and hence the results were representative for the entire sample.

For stainless steel welding aerosols the chromium oxidation state was determined separately. Two parallel membrane filters collect aerosol in the pipe of the welding aerosol sampling set-up, giving mass differences between the two samples of less than 5%. A sample thickness from 0.05 to 0.1 mg/cm^2 is optimal for the analytical methods applied. One of the filters was washed with de-ionized water buffered with a solution of $\text{NH}_4\text{NO}_3/\text{NH}_4\text{OH}$ to pH 7.4. One half of each filter, unwashed and washed respectively, was analysed with PIXE to determine the total and the less soluble chromium. The other halves of the filters were analysed with ESCA^{1,8} which determines the oxidation state of the chromium in a 2 nm thick surface layer of the particles. To evaluate if the ESCA results were representative, another pair of parallel samples was taken and the individual welding aerosol particles were studied by transmission electron microscopy. The buffer solution containing the chromium which has been leached out was analysed with spectrophotometry using the DPC-reagent (diphenylcarbazide)^{1,9}.

In the cascade impactor for particle size determinations glass plates (Casella, diam: 25 mm) were used. Prior to use, these were cleaned and dipped into a

solution of polystyrene in toluene, which was then drained through a valve, slowly and at a constant speed. After drying a $30 \mu\text{g}/\text{cm}^2$ thick polystyrene layer covered the plates. The plates were then placed 3 cm above a bath of melted hot paraffin (180°C) and the paraffin vapour allowed to condense on the plates for 15 min, forming a "sticky" layer to reduce "bounce-off" of particles²⁰. The glass plates were placed in the cascade impactor with the last four stages having 50 % cut-off diameters of 2, 1, 0.5 and $0.25 \mu\text{m}$, respectively, followed by an after-filter (Nuclepore, diam.: 25 mm, pore diam.: $0.4 \mu\text{m}$) to collect the smallest particles. After sampling, the plates were slowly put into de-ionized water and the polystyrene coatings with the aerosol samples floated off on to the surface of the water whence they were transferred to our standard aluminium frames. The latter were then mounted in the slide frames for subsequent proton irradiation for about 100–200 seconds, using a beam current of 50 to 150 nA and a 0.5 cm^2 beam area, sufficient to cover the samples completely. For the after-filter, the beam area was 0.13 cm^2 with a proton current of 30 to 50 nA and the analysis times from 200 to 300 seconds. Fluorine in the impactor samples was determined using the $^{19}\text{F}(\text{p}, \alpha\gamma)^{16}\text{O}$ reaction.

SAMPLING PROCEDURES

In Table 1 the different welding situations studied are summarized. The welding current was varied within the intervals recommended for each method and dimension by the manufacturer. The welding voltage was varied significantly outside "proper" welding conditions in order to show any possible systematic dependence of fume production on welding voltage.

Three to five collections were made for each set of welding parameters. The results are given as averages of the numbers of measurements made and the error limits given are one standard error of the mean. For some methods, e.g. GMAW on aluminium, only very restricted parameter intervals can be used for welding. The alternating current mode is recommended only for a few SMAW-methods and hence the influence of current mode on the welding aerosols has been studied for these methods only.

For the direct current SMAW-methods, an ESAB 400 welding generator is used in accordance with the instructions by the welding electrode manufacturer, i.e. reversed polarity (electrode positive). The welding is performed manually by a skilled welder exerting himself to maintain constant welding conditions.

Normally, the fumes from only one electrode are collected on one glass fibre filter but, to reduce weighing errors, for a few methods with very low fume emission several electrodes were welded. Current and voltage were recorded on a two-channel chart recorder. Voltage was measured between the electrode and the work piece and the current by a precision resistor in series with the welding generator. When AC-welding is carried out, a high current transformer was used.

For the GMAW-methods, an ESAB LBA 550 welding generator was used with the welding gun mounted in a fixed position perpendicular to the workpiece. The latter was clamped to an aluminium wagon running on rails with a very constant but variable speed to simulate the normal movement during welding. This automatic welding arrangement is necessary for the semi-automatic methods studied, since it is difficult to maintain constant conditions manually. Current and voltage were recorded in the same way as for the SMAW-methods. The wire feeding speed in GMAW-welding is adjustable and the setting was noted for each welding situation. They were calibrated by feeding the wire without welding for a certain time and measuring the amount of wire fed. The protective gas flow was monitored by a rotameter.

For GTAW-welding, a Miller DC welding generator is used. Due to the low emission rates from GTAW-processes, very long welding and collection times (30-40 min) were used.

The fans which pull air through the sampling pipe and the pumps for the membrane filter and the cascade impactor were all started before welding starts. After about 10 seconds of welding, the valves in the connections for the impactor are switched from clean air to welding aerosol collection, which continues for 20-40 seconds. The valves are then switched back and all the aerosol still inside the cascade impactor is allowed to be collected at nominal flow rates before the pump is turned off. About 20 seconds after finishing the welding, the fan and pump were turned off and the filters and impactor plates exchanged in a laboratory completely sealed-off from the welding hall.

RESULTS AND DISCUSSION

TOTAL FUME EMISSION

To facilitate comparison of fume production from different welding techniques, it is convenient to define two entities, viz. the total fume emission rate, E , the total mass of emitted fume in g/min, and the relative fume formation index, R , the total mass of emitted fume normalized to the mass of deposited consumable (excluding slag) in mg fume per g deposited consumable. In Table 2, the total masses of aerosols produced in the different welding processes, expressed in terms of E and R , are summarized. The results selected are for "normal" values of welding parameters and dimensions.

Electrode	Diam.(mm)	I (A) ¹	U(V) ¹	E(g/min)	R(mg/g)
OK 38.65	3.25	160	35	0.58	16.7 ³
OK 38.85	5	300	34	1.30	15.7
OK 38.95	4	210	32	0.93	21.7
OK 38.95 ²	4	205 ²	30 ²	0.75	19.2
OK 48.00	3.25	140	23	0.45	26.0
OK 61.41	3.25	115	33	0.38 ³	11.3 ³
OK 63.35	4	140	24	0.39	15.6 ³
OK 69.21	4	140	22	0.29	12.4
OK 12.51 CO ₂	1.2	180	30	0.23 ⁴	5.4 ⁴
OK 16.32 Ar	1.2	180	26	0.20	3.8
OK 16.32 Ar/CO ₂	1.2	180	26	0.29 ³	5.7
OK 18.01 Ar	1.2	180	22	0.49	20.5
OK 18.13 Ar	1.2	160	24	0.91	24.1
Tungsten, thoriated	-	112	12	0.002	-

1) Direct current; reversed polarity (electrode as anode).

2) Alternating current.

3) Standard error of the mean : 5-10%.

4) Standard error of the mean : 10-15%.

Table 2. The welding situations referred to in the text as "normal" welding, implying that the welding currents were chosen to be in the middle of the intervals recommended by the manufacturers and the welding voltage close to the values recommended. E and R denote respectively the fume emission rate and the relative fume formation index. The standard errors of the mean were less than 5% if not given.

The total fume emission rate is very dependent on electrode dimension and electric power and, due to variation in these parameters, E varies in the interval 0.2 to 2 g/min for the methods in the present study (except for GTAW). As can also be seen from Table 2, large variations in R are found between the different methods (3-35 mg/g). The choice of welding method will strongly influence the ratio between fume production and welding production. However, since this choice is guided also by technical demands and availability and since the comparison does not include the chemical composition of the welding aerosol, it is not always possible or even desirable to choose the method of lowest relative fume formation index. From Table 2 can be inferred that the SMAW methods generally give higher values of both E and R than the GMAW methods. One exception, however, is GMAW for aluminium welding with equally high or even higher values than SMAW.

The results in Table 2 can be compared with those of the systematic study in ref.². The methods in this study with a corresponding or very similar method as in ref.² are OK 48.00, OK 61.41, OK 63.35, OK 12.51, OK 16.32 and OK 18.13. Both E and R for these methods are in good agreement with the results in ref.², the differences being normally smaller than 10%. The discrepancies might be explained by somewhat different welding conditions and variations between different brands of welding consumables of the same classification.

SMAW

In Table 2 are given emission results for "standard" welding situations recommended by the the manufacturer. However, when the welding current is raised within the intervals recommended, there will be a significant increase of E reflecting the enhanced melting rate of the consumable. This current dependence seems similar for all SMAW-methods and in fig 5 the fume emission rate is plotted versus welding current (at normal welding voltage). All the methods, dimensions and currents studied are included and it seems that E might be expressed mathematically as $E = a \cdot I^b$. Regression analysis of this power curve gives $a = 2.1 \cdot 10^{-4}$ and $b = 1.54$ with $r^2 = 0.88$, indicating a strong dependence of E on current. Since all the data points in fig 5 lie close to the regression line, the seven SMAW-methods in this study, despite their different dimensions, coatings and core compositions, seem to follow approximately the same current dependence when they are used according to the manufacturer's recommendations. These results agree well with those of refs.² and ²¹.

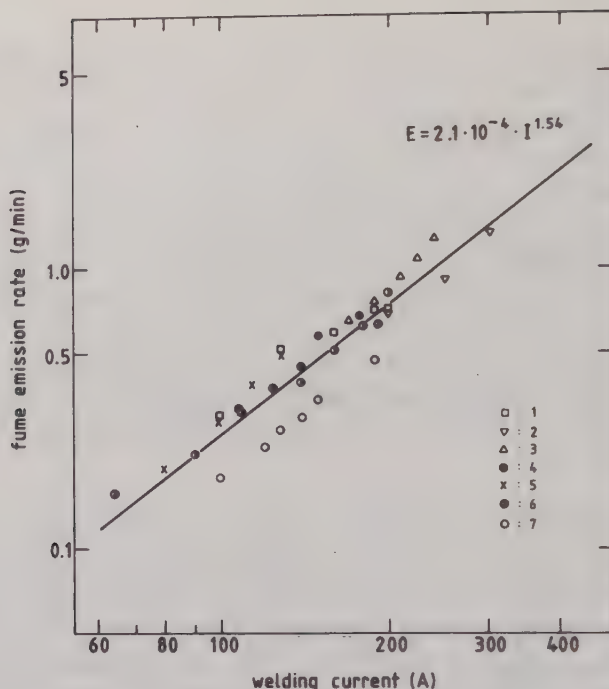


Figure 5. Fume emission rates for all the SMAW-methods in this study plotted versus welding current ($r^2=0.88$). The number at each symbol refers to the corresponding welding method in Table 1.

For the relative fume formation index R , the influence of welding current is, within the stated current interval, normally rather low, since the increased fume emission rate is mainly the result of an increased melting rate. For some methods, a slight increase in R with current is found, probably because of the increased temperature at the melting tip of the electrode.

In fig. 6 and 7 the fume emission rate and the relative fume formation index of three different SMAW methods (for stainless steel) are plotted versus welding voltage. Increases in both E and R are observed with increasing voltage. At high voltage the long electric arc creates increased turbulence and hence facilitates penetration of oxygen through the protective atmosphere formed by the evaporating electrode coating. This oxygen can react with the melted and vapourized metals forming oxides which will promote fume emission since they often have higher vapour pressure than the pure metals. From fig. 7, it is evident that the influence of welding voltage on R is dependent of the type of

coating on the electrode in question. Different relations between voltage and arc length are the probable explanation for this. The crater formed by the coating during steady state welding hides part of the electric arc and hence it is very difficult to measure the arc length for direct correlation with R. Since the use of a longer arc causes increased disturbance due to metal spatter and turbulence it also produces a deteriorated welding joint. Hence, keeping the arc length short and welding voltage low, e.g. by keeping the angle between the electrode and the work piece close to 90° ²¹, should be recommended.

The SMAW methods in this study have normally been welded with DC and reversed polarity. For one method, however, AC is also recommended and in Table 2 E and R are given for this method for both modes of current. The values of E and R are somewhat lower in the case of alternating current but the differences (<10%) are insignificant from the hygienic point of view.

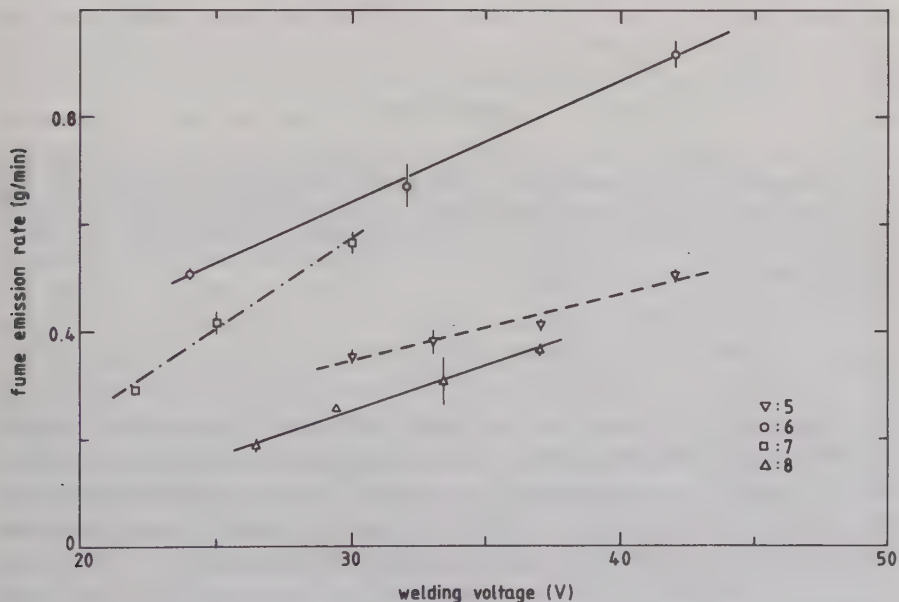


Figure 6. Fume emission rates for three SMAW-methods (stainless steel welding) and for the GMAW method with CO_2 as protective gas (mild steel welding) plotted versus welding voltage. The number at each symbol refers to the corresponding welding method in Table 1. The welding currents were 115, 160 and 140 A for methods 5, 6 and 7 respectively, and 200 A for method 8. The error bars show one standard error of the mean.

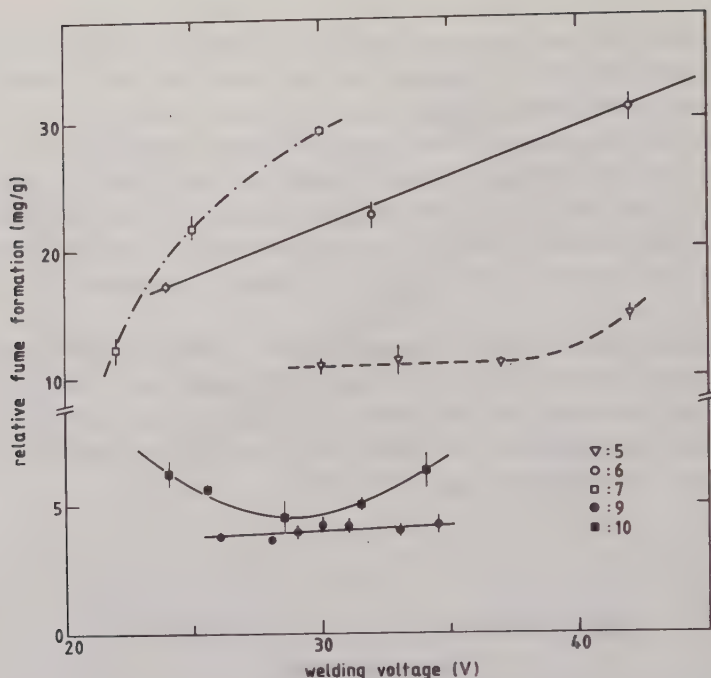


Figure 7. Relative fume formation index plotted versus welding voltage for the same SMAW methods as in fig. 6 and for the GMAW method with pure Ar (●) and Ar/CO₂ (■) as protective gases respectively. The number at each symbol refers to the corresponding method in Table 1. The welding current in method 10 was 180 A. The error bars show one standard error of the mean. Note the shift of scale on the ordinate axis.

GMAW

Semi-automatic methods for gas metal arc welding may appear to be well-controlled and simple physical systems composed of the melting metal wire and the surrounding protective gas. However, due to the influence of the protective gas on the electric arc and on the metal transport process, the fume emission will be a complex function of the welding parameters.

When pure CO₂ is used as a protective gas, the transfer of the melted metal from the electrode tip to the work piece can be characterized as large globules (diameter: 2 to 3 mm) transported by gravity and magnetic forces. The sizes of the globules are virtually unchanged when the welding parameters are altered. If, however, the protective gas is argon or mixtures of argon and CO₂, two different modes of transfer will be possible. With low voltage and low current the transfer will be globular with decreasing sizes and increasing numbers of

globules for increasing current. For high voltage, at a certain critical value of current, the transition current, a very abrupt change in the size and frequency of the globules takes place and metal transfer becomes a spray of very small droplets (diameter: 0.5-1 mm). The drop size remains rather constant when the current is increased and instead the number of droplets per unit time increases. The detachment of the small droplets from the electrode is due partly to the magnetic "pinch effect" and transport along the arc is due mainly to the plasma jet²². The value of current at which this transition occurs is proportional to the diameter of the electrode and dependent on the material and electrode extension²³.

When mixtures of argon are used, the gas with which it is mixed changes the properties of the protective atmosphere and hence the fume formation process will be altered. In fig 7 the relative fume formation index is plotted versus welding voltage with pure argon and with a mixture of 80% argon and 20% CO₂ as protective gases, respectively. While, for pure argon, R is rather independent of the welding voltage, there is a well-defined minimum at a specific voltage for the Ar/CO₂ case. The magnitude of R is also higher for all voltages when CO₂ is mixed into the gas and hence the oxidizing potential of the atmosphere surrounding the arc is increased. The oxides of several elements have higher vapour pressure than the pure elements, thus promoting fume formation in a oxidizing atmosphere. This effect has been shown in detail in refs. ³ and ²⁴.

The welding current for OK 16.32 in fig.7 ($I=180\pm 5$ A) is above the transition level for this particular electrode with a diameter of 1.2 mm²⁵. To establish a stable spray arc, the voltage (arc length) has to exceed a certain value, which in the case of pure argon was about 30 V and for the Ar/CO₂ mixture 28 V. The minimum in R in fig.7 for the Ar/CO₂ mixture coincides with the lowest voltage at which a stable spray arc can exist. Once a stable spray arc is established, R will increase with voltage in case of Ar/CO₂ gas but remain constant for pure Ar. The increased voltage corresponds to a longer electric arc with a consequently longer residence time for the droplets in the oxidizing atmosphere while being transferred to the work piece, and hence, according to what is stated above, an increased probability for fume formation. The inert Ar-atmosphere which surrounds the arc protects the droplets from oxygen during transfer and essentially all fume will be produced, mainly due to vaporization, close to the melting tip where the temperature is very high.

In pure CO_2 -welding the fume emission rate increases strongly with voltage, as can be seen from fig.6. This dependence is in good agreement with the results of refs.²⁶ and ²⁷, where the same or very similar welding parameters have been used. If, instead, the welding current is increased at constant voltage, the wire feeding speed increases with a decreasing length of the welding arc²⁶. In fig 8 the relative fume formation index versus current is plotted for constant voltage. Due to the decreasing transition time for the globules in the CO_2 -atmosphere, R decreases with increasing current (compare ref³).

It is evident from the findings above that gas metal arc welding constitutes a complex field as far as the emission of welding fumes is concerned and that all welding parameters and conditions have to be stated precisely for adequate comparison of research results and finally that the choice of shielding gas has a significant influence on the fume emission characteristics.

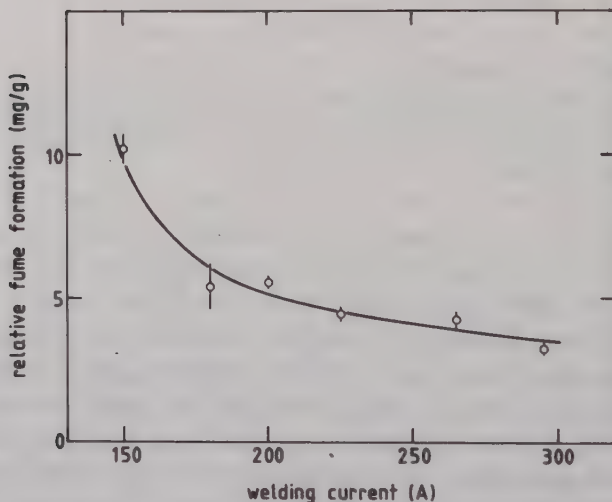


Figure 8. Relative fume formation index plotted versus welding current ($U=30$ V) for GMAW welding of mild steel with CO_2 as protective gas. The error bars show one standard error of the mean.

ELEMENTAL COMPOSITION

In Table 3, the elemental composition of welding aerosols from the different welding processes are given for the same parameter values as those in Table 2. The part of the aerosol which has not been analysed contains such elements as oxygen, nitrogen, sodium and silicon.

E l e m e n t s

	F	Cl	K	Ca	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Rb	Zr	Mo	Pb
No. ¹																
1	7.1		8.8	2.6		.07	5.9	32		.08	.17 ³	.06 ³		.54		.10 ³
2	11	.26 ³	15	.62	.54		4.7	24			.29 ⁴					
3	11	.33 ³	15	2.0			3.4	23			.04 ³			.23 ³		.07 ³
3 ²	14	.54 ³	19	1.8			2.8	11			.04 ³			.36 ³		.07
4	16		16	9.5	.45	.04	3.7	19		.01	.13	.03 ³				
5	21		18	1.3	2.1	3.4	2.4	3.7	.22	.01	.25		.02			
6	24	.34	22	10	.62	3.1	2.7	3.3	.24		.11		.01		.03	.03
7	16	.20	22	3.5	2.3	3.0	14	3.4	.44 ³		.14				.09 ³	.04 ³
8						.07 ⁴	7.3	45		.26 ³	.04 ⁴					
9						10	5.3	28	4.5	.06	.17				.95	
10						12	4.8	31	4.8	.09	.18				.92	
11						.02 ⁴		.12 ⁴		.03						
12						.04	.14	.06			.02					

1) See Table 1; 2) Alternating current; 3) Standard error of the mean : 10-20%

4) Standard error of the mean : >20%

Table 3 . Relative elemental compositions (expressed as a per cent of the total mass of aerosol) of the welding fumes from the welding situations described in Table 2 as determined by PIXE analysis. The standard errors of the mean are less than 10% if not explicitly shown. Due to its low total emission GTAW is not included.

Basically, the elemental composition of a welding aerosol reflects the composition of the consumable electrode used insofar that the elements present in the welding consumable are also found in the aerosols but normally with their relative abundances altered. In the electric arc column the highest temperature is found at the axis near the melting tip of the electrode²⁸. Consequently, metal vapours will come mainly from the welding electrode and from the surface of the metal droplets being transferred in the arc. This statement is supported by the findings in ref.²⁹ in which a systematic study was carried out to

determine the site of aerosol production in SMAW-methods. Known concentrations of chromium, manganese and nickel were added to coating, core wire and workpiece respectively. By elemental analysis of the welding aerosol the contributions from the different sites were estimated, and the core wire was found to be the dominating source of these metals in the aerosol. One consequence of this finding is that the choice of work piece composition is not very critical in welding aerosol studies. It is, however, very important to check that no surface contaminations, such as metal primers, are present since they may be much more volatile and will contribute significantly although they emanate from the low temperature zone of the arc.

In Table 4 are given fractionation factors of the different metals in the welding aerosol relative to the welding consumable for four different welding methods. Noticeable are the high factors for manganese (2-7) while the factors of the other elements are well below unity. This is in good agreement with the results from the above study^{2,9}. Since manganese has a much higher vapour pressure than, e.g. chromium and nickel, it will also have a higher tendency to fume formation and occur in relatively higher concentrations in the welding fumes as compared to the work piece.

<u>Shielded metal arc welding</u>		<u>Gas metal arc welding</u>	
Low alloy electrodes (n=4)	Stainless steel electrodes (n=3)	CO ₂ - gas Low alloy steel (n=1)	Argon - gas Stainless steel (n=2)
Cr	0.17-0.21		0.68-0.70
Mn 2.2-6.1	2.3-3.8	6.9	4.2-5.2
Fe 0.22-0.33	0.055-0.066	0.49	0.47-0.50
Ni	0.025-0.040		0.36-0.41
Mo	0.027-0.052 (n=2)		0.24-0.32

Table 4. The elemental concentrations in the fumes divided by the elemental concentrations in the welding consumables. The intervals are defined by the minimal and maximal values. n = the number of methods included.

SMAW

The welding parameters, mainly the voltage, affect the elemental composition of the welding aerosol. In fig.9 are plotted the relative abundances of five different elements in the fume from a stainless SMAW-method versus welding voltage, showing increasing concentrations for the three core wire metals chromium, manganese and iron and decreasing concentrations of fluorine and potassium which originate from the electrode coating. For other electrodes, the voltage dependence is not exactly the same, but nevertheless the same groups of

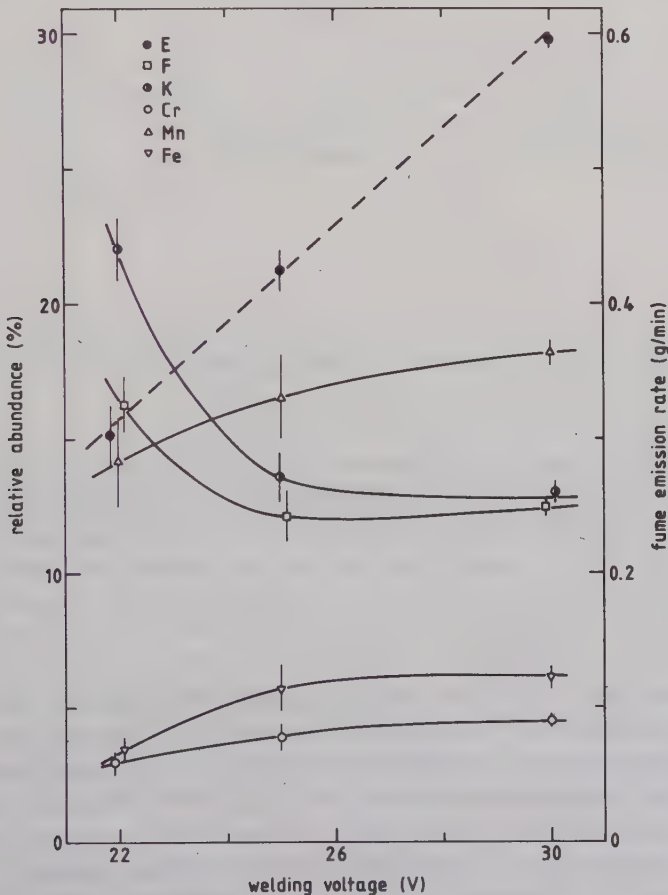


Figure 9. Relative elemental abundances (left-hand axis) in the fumes from welding stainless steel with a SMAW-method (OK 69.21, diam.:4 mm and I=140 A) plotted versus welding voltage. To facilitate estimating the absolute elemental emission, E is also plotted (right-hand axis). The error bars show one standard error of the mean.

elements develop, e.g. potassium and fluorine represent one category of elements following similar patterns of variation and chromium, manganese, iron and nickel normally another. The reasons for these variations may be the resemblance in chemical and physical properties and/or in the distribution of the elements in the electrode. The distinct voltage dependence of the elemental composition is probably explained by the variation in arc length. In fig.9 the dependence of the fume emission rate on voltage is also included in order to show how the absolute emissions of these elements vary with voltage.

Welding is normally performed in the DC mode and with reversed polarity but in some methods AC is also used. For one of the methods studied here, the change to AC causes a drastic change in the relative composition (compare Table 3). The temperature at the electrode tip depends on the polarity and consequently the use of an alternating current is expected to change the conditions for fume production and hence the chemical composition.

GMAW

In the semi-automatic GMAW-methods no protective electrode shielding is used and the composition of the welding fumes is determined by the composition of the metal wire and by the protective gas.

Gas metal arc welding of mild steel is normally performed in a 100% CO₂ atmosphere giving globular transfer as described above. When the welding parameters are varied, no significant variation in the elemental composition has been observed in the present study. This and the relative abundances of Mn and Fe observed are in good agreement with the results from other studies of the same process^{3,30}.

It was shown above that a protective atmosphere of argon affects the fume emission characteristics since metal transfer varies with welding parameters. In fig 10, it is shown that the same effect is found in the elemental composition. The relative abundances of two elements in the fume during the welding of stainless steel are plotted versus welding voltage (100% Ar = o, Ar/CO₂ = □). To allow estimates of the absolute mass emissions of the elements, the fume emission rate is also plotted. All metals except manganese have higher relative abundance with Ar/CO₂ than with pure Ar. For both protective gases, the general trend for both elements is to increase with voltage. However, in pure Ar gas, a

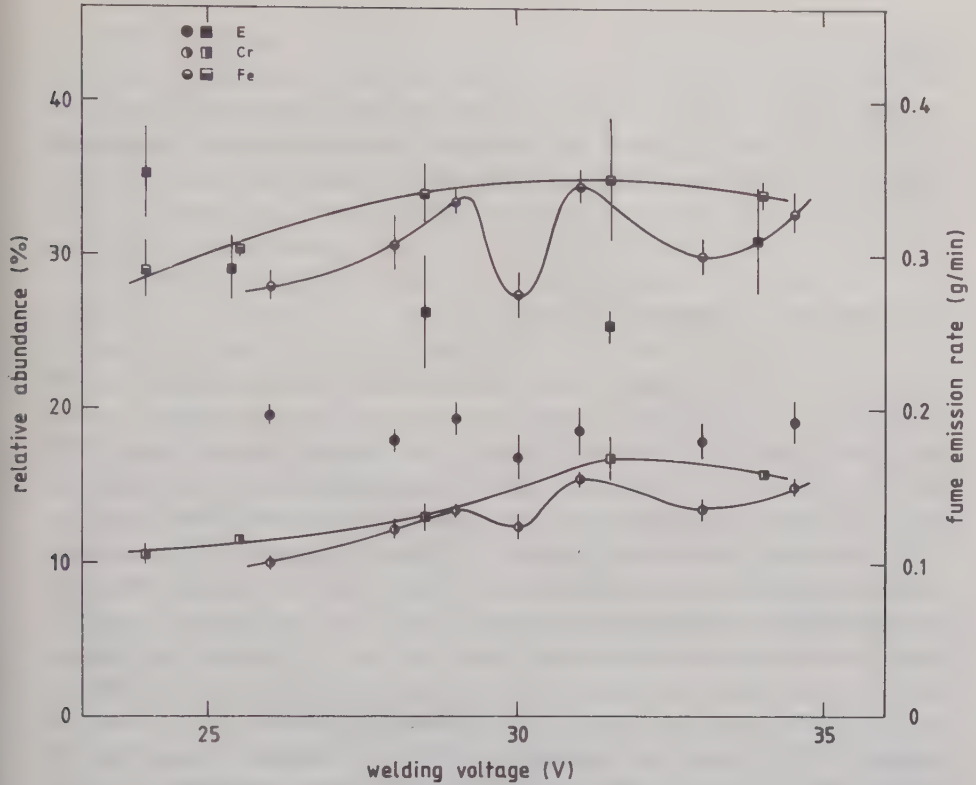


Figure 10. Relative elemental abundances (left-hand axis) in welding stainless steel with GMAW (OK 16.32, I=180 A) and 100% Ar (○) and Ar/CO₂ (□) as protective gases, respectively, plotted versus welding voltage. To facilitate estimating the absolute elemental emission, E is also plotted (right-hand axis). The error bars show one standard error of the mean.

fine structure with dips in the relative abundance at the lowest voltage (approx. 30 V) at which a stable spray transfer can exist is noticed. A similar dip is not observed at the corresponding voltage (approx. 28 V) in the case of Ar/CO₂. A tentative explanation for this fine structure and the difference between the gases is the establishment of a very stable arc essentially free from spatter and turbulence at a critical voltage, assuming the current is high enough, i.e. above the transition current. When pure Ar is used, the oxidizing agents come primarily from the surrounding air and their penetration is significantly reduced because of the very stable arc. With 20% CO₂ in the gas, the oxygen in CO₂ will be the dominant oxidizing agent and the influence of the surrounding air is less pronounced.

GTAW

Since the total fume emission is very low for GTAW and pure Ar as the protective gas, no results on the elemental composition of the aerosols formed are included in Table 3. However, apart from Fe, Mn, Cr, Ni, Cu and Zn, traces of W are also found.

OXIDATION STATE OF CHROMIUM

An analytical routine developed for determinations of chromium oxidation state^{1 5} was applied to stainless steel welding aerosols from three SMAW-methods and one GMAW-method. The results are shown in Table 5. For GTAW of stainless steel, the total fume emission was too low for this analytical procedure to be used. In aerosols from the three SMAW-methods for stainless steel welding, more than 50% of the chromium is soluble and hexavalent. Between 60 and 100 % of the chromium in the particle surface layers is hexavalent as determined by ESCA-analysis, but decreases after washing the aerosol with a buffer solution (pH 7.4). Apparently most of the hexavalent chromium on the particle surfaces leaches out during washing. The formation of hexavalent chromium is dependent on which elements have been added to the coating and it has been shown by Kimura et al^{3 1} that it is possible to reduce the amounts of hexavalent chromium by changing the additives to the coatings and still perform technically adequate welding.

Method number ¹	Diam. (mm)	I(A)	U(V)	Cr-tot (%)	A	B	C
5	3.25	100	35	3.4	.50	.60	.27
6	3.25	100	22	4.4	.73	1.00	< .15
7	3.25	105	21	2.9	.52	1.00	< .15
9	1.2	180	26	12	.019	< .15	< .15

1)= see table 1

A = Cr(IV)-soluble/ Cr-total.

B = Cr(VI)/Cr-total on the particle surfaces.

C = Cr(VI)/Cr-total on the particle surfaces after washing.

Table 5. Results from determinations of oxidation state and solubility of chromium in welding aerosols from stainless steel welding.

Transmission electron microscopy (TEM) gives information on the structure of individual welding particles for interpreting the ESCA-results. The aerosol particles from the SMAW methods appear as chains or agglomerates of smaller particles ($<0.1 \mu\text{m}$ in geometric diameter). The chains are surrounded by shells with lower electron density than the particles in the core. The ESCA analysis of unwashed particles is just valid for the outer layer of these shells. After washing, a large fraction of the shell has been dissolved and information on the core material is obtained from ESCA. The TEM studies have shown that after washing, the core particles consist of smaller homogeneous particles with diameters of about $0.01 \mu\text{m}$. The ESCA results are representative of about 80% of the volume of particles of this size.

The washing procedure separates the readily soluble Cr from less soluble, in a well-defined way. However, from the toxicological point of view, the separation of these fractions is not well-defined, because of the uncertainty of the hygienic significance of differences in the solubilities of various chromium compounds. In a particle of welding aerosol, the chromium is present in a complex environment and the solubility found in the washing procedure may not, in a simple way, be relevant to the solubility of a given chromium compound in the airways.

Chromium oxidation state results for argon gas metal arc welding are quite different from SMAW-results. Only about 2% of the total chromium is soluble and hexavalent and for both the unwashed and washed aerosol samples the concentrations of hexavalent chromium on the particle surfaces are below the detection limit of the ESCA method ($<15\%$).

The results indicate that, although the aerosols from them have lower relative abundances of total chromium, the use of SMAW-methods would imply significantly higher health hazards than the use of GMAW-methods. Switching to the latter methods, however, may not always be possible for technical reasons. Further, when comparing the health hazards of these two classes of welding, other aspects, such as the hazardous gases emitted during welding have to be taken into consideration. In most processes NO_x is formed and in GMAW and GTAW also considerable amounts of the strong irritant ozone (O_3). Discussions or measurements of these gases have been beyond the scope of this study and hence the conclusions about possible health effects of the SMAW, GMAW and GTAW processes reached here do not include the influence of hazardous gases formed during welding.

Within the uncertainties of the differences in welding conditions and parameters, the results about the content and oxidation state of chromium in welding aerosols found here are consistent with those of other studies^{3 2-3 4}.

PARTICLE SIZE DISTRIBUTION

In Table 6 the mass median aerodynamic diameters (MMAD), as determined by the Battelle cascade impactor, are summarized. A typical value of the geometrical standard deviation of the distributions is 1.5. The MMAD-values are calculated from PIXE-analysis of the impactor stages and expressed as the MMAD for each element separately. In the case of gas tungsten arc welding the particles are so small that about 75% of the detected mass is found on the after-filter of the impactor and the MMAD value is thus less than 0.25 μm which is the 50% cut-off diameter of the last impaction stage. The mass median aerodynamic diameters for the other methods vary from 0.3 μm to about 0.6 μm . Hence the particles are respirable and have a high probability of deposition in the lower parts of the

Mass median aerodynamic diameter (μm)

Electrode	F	Al	K	Ca	Ti	Cr	Mn	Fe	Ni
OK 38.65	.34		.32	.36			.33	.33	
OK 38.85			.45				.45	.45	
OK 38.95			.48				.48	.48	
OK 48.00	.48		.50	.44	.50		.46	.44	
OK 61.41			.39	.43	.39	.38	.39	.39	.35
OK 63.35			.39	.39		.39	.39	.42	
OK 69.21						.47	.49	.30	
OK 12.51 ¹							.32	.33	
OK 16.32 ²						.31	.30		.32
OK 16.32 ³						.34	.34	.35	.34
OK 18.01 ²		.42							
OK 18.13 ²		.37							

1) 100% CO₂; 2) 100% Ar; 3) 80% Ar and 20% CO₂

Table 6. Mass median aerodynamic diameter for different elements and welding methods as determined by the Battelle cascade impactor and PIXE analysis.

respiratory tract. In other welding aerosol studies, only a few particle size distribution determinations have been reported. The results of refs.^{2-5,9,27} are essentially in agreement with those of the present study. The low MMAD values found in GTAW indicate that the high arc temperatures in this type of welding (approx. 10000 K) together with the basically non-melting electrode, made from thoriated tungsten, promote the formation of very small particles.

The particles emitted in SMAW-methods contain significant concentrations of highly soluble and hygroscopic compounds derived from elements such as F, K and Na in the electrode coating. The high relative humidity of the human respiratory tract, $RH > 99\%$ in the subglottic region³⁵, makes the particles rapidly absorb water, which may significantly alter the patterns of deposition there.

Particle size determinations have been carried out for all methods and sets of parameters. When the welding parameters are changed, only negligible variations ($<10\%$) of the particle diameter will occur. The variation of the MMAD between elements for a certain method is also negligible. The particle formation process normally includes evaporation, oxidation and condensation steps³. The process has been shown to be sensitive to the welding parameters in producing different compositions and mass concentrations but apparently this is not reflected in the particle sizes, but rather in the number concentration of the aerosols. One important implication of these results is the possibility of using a simplified method to characterize welding aerosols including only a few particle size determinations for each method. The particle size determination is rather tedious and complicated insofar as sampling and analysis are concerned and a reduction in the number of determinations will save substantial time and effort.

SUMMARY

Several welding methods were characterized using a specially designed collection apparatus which has been found to be reliable and to yield accurate and representative sampling of welding aerosols. Special requirements of very low air velocity around the welding place and the possibility of testing the GMAW methods in automatic mode excluded the use of the standardized "Swedish fume box"³⁶. The analytical facility of Particle Induced X-ray Emission was a prerequisite for this extensive and detailed study. The PIXE method, with complementary nuclear methods, is very well suited to the study of work environment aerosols in general¹⁴ and welding aerosols in particular, in that it yields complete quantitative information of many important elements at a low cost. Furthermore, as compared to traditional techniques it significantly simplifies particle size determination.

The highest fume emission in this study is found for SMAW methods followed by GMAW of aluminium and GMAW of steel. By far the lowest emission is found for GTAW of stainless steel. The fume emission rate (E) is determined primarily by the welding current and a similar current dependence is found for all SMAW methods if welded at normal voltage. The voltage also affects E but to a smaller extent. The relative fume formation index (R) varies drastically among the methods and is dependent on the welding parameters. For gas metal arc welding of mild steel with pure CO₂ as the protective gas, R decreases with increasing current.

The composition of the shielding gas in GMAW is important for the fume production. R is higher in the case of the Ar/CO₂ mixture than in the case of pure Ar. The influence of the welding parameters on fume formation is altered by mixing CO₂ into Ar. This study supports the findings of earlier works, viz. that the oxidizing potential of the gas surrounding the electric arc is of considerable importance in determining the fume production, with increased fume production when increasing the oxidation potential of the protective gas.

The elemental composition of a welding aerosol is dependent on the method but also on the welding parameters, primarily the voltage. The fume contains the same elements as does the consumable but with the relative abundances changed due to fractionation effects during aerosol formation. This is explained by the different properties of the elements, e.g. with regard to vapour pressures of the pure elements and their compounds. For SMAW with the recommended voltage,

only minor variations occur when the current is changed. Welding voltage and current mode (AC/DC) have drastic impacts on the elemental composition of the fumes. This is probably due to changes in electric arc length and arc characteristics respectively. The elemental composition of a GMAW aerosol is also dependent on the protective gas. Thus, a relative decrease in several elements is noted when the transition from globular to spray transfer takes place in an Ar atmosphere. The complexity of fume formation processes and the growing popularity of GMAW methods in industry due to increased production and welding quality stresses the need for further studies within this field.

The fumes produced from SMAW and GMAW methods when welding stainless steel clearly show the great differences between these two main types of welding procedures. While the chromium in the SMAW aerosols is almost entirely hexavalent (and soluble), only trivalent chromium is found in the GMAW aerosols. The well-known difference in biological activity between the two oxidation states of Cr is reason enough to infer that, if possible, GMAW methods should be chosen when welding stainless steel.

The particles in the welding aerosols are below 1 μm in diameter and consequently respirable and able to reach the lower parts of the human respiratory system. Mass median aerodynamic diameters vary from well below 0.25 μm to 0.6 μm and seem to be rather independent of the welding parameters. An important factor in evaluating the deposition of aerosols from SMAW methods is the hygroscopicity of the particles which, in the high humidity of human airways, may cause changes in the aerodynamic properties of the particles.

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